OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETALDEHYDE

INTRODUCTION

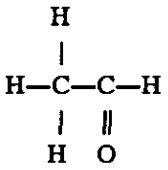
This guideline summarizes pertinent information about acetaldehyde for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CH_3CHO

- **Structure**



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- **Synonyms**

Acetic aldehyde, ethanal, acetylaldehyde, ethyl aldehyde

- **Identifiers**

1. CAS No.: 75-07-0
2. RTECS No.: AB1925000
3. DOT UN: 1089 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

Acetaldehyde is a colorless, flammable, volatile liquid or gas (above 69°F) with a pungent, fruity odor detectable at low concentrations. The odor threshold is reported to be between 0.05 and 2.3 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44.1
2. Boiling point (at 760 mm Hg): 21°C (69.8°F)
3. Specific gravity (water = 1): 0.79 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetaldehyde): 1.5
5. Melting point: −123.5°C (−190.3°F)
6. Vapor pressure at 20°C (68°F): 740 mm Hg
7. Solubility: Miscible with water, alcohol, ether, acetone, benzene, gasoline, solvent naphtha, toluene, turpentine, and xylene
8. Evaporation rate (ether = 1): 3

- **Reactivity**

1. Conditions contributing to instability: Contact of acetaldehyde with air may cause the formation of explosive peroxides, and contact of this substance with heat or flame may cause fires or explosions. Contact with trace metals or alkaline materials may cause acetaldehyde to undergo hazardous polymerization.
2. Incompatibilities: Fire and explosion may result from contact of acetaldehyde with strong oxidizers. Acetaldehyde reacts vigorously with acid anhydrides, alcohols, anhydrous ammonia, amines, ketones, phenols, hydrogen cyanide, hydrogen sulfide, halogens, phosphorus, isocyanates, and strong alkalies.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and methane) may be released in a fire involving acetaldehyde.
4. Special precautions: Liquid acetaldehyde attacks some coatings and some forms of plastic and rubber.

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- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to acetaldehyde.

1. Flash point: −37.8°C (−36°F) (closed cup)

2. Autoignition temperature: 175°C (347°F)

3. Flammable limits in air (% by volume): Lower, 4.0; upper, 60.0

4. Extinguishant: Use dry chemical, carbon dioxide, or alcohol foam to fight fires involving acetaldehyde. Water may be ineffective, but it may be used to keep fire-exposed containers cool and to protect persons attempting to stop the leak. If a leak or spill of acetaldehyde has not ignited, water spray may be used to disperse vapors.

Fires involving acetaldehyde should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetaldehyde may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetaldehyde. Firefighters' protective clothing may provide limited protection against fires involving acetaldehyde.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Adminstration (OSHA) permissible exposure limit (PEL) for acetaldehyde is 100 ppm (180 mg/m^3) as an 8-hr TWA concentration and 150 ppm (270 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure which should not be exceeded at any time during the working day [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers acetaldehyde to be a potential occupational carcinogen and recommends exposures be controlled to the lowest feasible limit [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned an acetaldehyde threshold limit value (TLV) of 100 ppm (180 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 150 ppm (270 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of conjunctivitis and sensory irritation of the respiratory tract associated with exposure to acetaldehyde. The NIOSH limit is based on positive carcinogenic results in animal studies.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetaldehyde can occur through inhalation, ingestion, or contact with the eyes, skin, or mucous membranes.

- **Summary of toxicology**

1. *Effects on Animals*: Acetaldehyde is an irritant of the eyes, mucous membranes, and upper respiratory tract in animals; at high concentrations, it is a central nervous system depressant. Acetaldehyde has caused squamous cell carcinomas and adenocarcinomas of the nasal cavity in rats and hamsters; it is also embryotoxic and teratogenic in several species of animals. Acetaldehyde causes severe irritation when applied to the eyes of rabbits; it causes mild irritation in contact with skin [NIOSH 1991]. In rats, the oral LD_{50} is 661 mg/kg, and the LC_{50} is 37 g/m^3 (20,550 ppm) for 30 min [NIOSH 1991]. Cats exposed to 380 ppm for 7 hr showed no effects; but increasing the concentration to 1,520 ppm caused signs of respiratory tract irritation [ACGIH 1991a]. Rats exposed to concentrations ranging from 400 to 5,000 ppm for 6 hr/day, 5 days/week for 4 weeks showed slight degeneration of the nasal epithelium at 400 ppm, and growth retardation, increased urinary output (in males only), and slight-to-moderate degeneration (with or without hyperplasia and metaplasia) of the nasal epithelium at 1,000 or 2,200 ppm [IARC 1985]. The rats exposed to 5,000 ppm showed severe growth retardation, increased neutrophil counts, reduced urine volumes, increased lung weights, and severe degenerative hyperplasia and metaplasia of the nasal, laryngeal, and tracheal epithelium [NLM 1992]. Hamsters were exposed to acetaldehyde concentrations ranging from 390 to 4,560 ppm for 6 hr/day, 5 days/week for 90 days. At the lowest concentration, these animals showed no toxic effects; at the highest concentration, however, they showed signs of eye and nose irritation, growth retardation, and erythrocytosis. At autopsy, these high-dose animals showed

increased kidney and heart weights and severe histopathologic changes of the respiratory epithelium [IARC 1985]. Fetal malformations (facial and cranial), digital anomalies, and embryonic deaths (resorptions) occurred in the offspring of rats and mice from dams treated with acetaldehyde during pregnancy [IARC 1985]. Acetaldehyde has been tested for carcinogenicity in rats by inhalation and in hamsters by inhalation and intratracheal administration. In rats, inhalation of acetaldehyde caused a statistically significant increase in the incidence of nasal adenocarcinomas and squamous cell carcinomas of the lungs. In hamsters, inhalation caused a significant increase in the incidence of laryngeal carcinoma, and intratracheal injections resulted in the induction of "peribronchiolar adenomated lesions," which were apparently not classified as tumors. The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence for the carcinogenicity of acetaldehyde in animals [IARC 1987]. Acetaldehyde is mutagenic in bacterial and mammalian test systems with and without activation [NIOSH 1991].

2. *Effects on Humans*: Acetaldehyde is an irritant of the eyes, mucous membranes, skin, and upper respiratory tract, and it is a central nervous system depressant in humans. On the basis of effects seen in animals, acetaldehyde is a potential carcinogen in humans. Although sensitive individuals experienced irritation when exposed to 25 ppm for 15 min, most unacclimated human volunteers exposed to 50 ppm experienced mild eye irritation, and all subjects exposed to 200 ppm developed conjunctivitis [Proctor et al. 1988]. Upper respiratory tract irritation was reported at a vapor concentration of 134 ppm [Proctor et al. 1988]. Eye contact with liquid acetaldehyde causes a burning sensation and superficial corneal injury; exposure to concentrations above 50 ppm may cause persistent tearing, photophobia, and injury to the corneal epithelium [Grant 1986]. Acetaldehyde causes erythema when splashed on the skin; if contact is repeated or prolonged, this substance may cause dermatitis or skin burns [Proctor et al. 1988]. A study of East German workers exposed to acetaldehyde and other chemicals in a chemical factory showed an increase in the number of cancers of the bronchial tubes and oral cavity. However, IARC has concluded that the results of this study are inconclusive because the workers were exposed to other chemicals and only a small, poorly defined population was involved [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetaldehyde can cause irritation of the eyes with burning, conjunctivitis, tearing, blurred vision, and photophobia; irritation and burning of the nose with rhinorrhea; and irritation of the upper respiratory tract with pain and coughing. Exposure to high levels of this substance may cause headache, drowsiness, dizziness, excitement, and agitation, followed by narcosis or stupor, pulmonary edema, and possibly death resulting from respiratory failure; however, ingestion can also induce nausea, vomiting, and diarrhea. Skin contact may cause dermatitis and burns of the exposed area.

2. *Chronic exposure*: Chronic exposure to acetaldehyde can cause conjunctivitis, coughing, difficult breathing, and dermatitis. On the basis of effects seen in animals, chronic exposure to acetaldehyde may cause heart and kidney damage, embryotoxicity, teratogenic effects, and possibly cancer in humans.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetaldehyde. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetaldehyde are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetaldehyde or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetaldehyde and may result in worker exposures to this substance:

- Synthesis of acetic acid, acetic anhydride, acrolein, aldol, butanol, butylene glycol, chloral, crotonaldehyde, 2-ethylhexanol, metaldehyde, paraldehyde, pentaerythritol, peracetic acid, pyridines, and trimethylolpropane
- Manufacture of synthetic resins, aniline dyes, herbicides, fungicides, other pesticides, explosives, and pharmaceuticals
- Synthesis of rubber processing chemicals, disinfectants, cosmetics, and perfumes
- Use of acetaldehyde in silvering mirrors and as an alcohol denaturant
- Use of acetaldehyde as a hardening agent in photography and in the manufacture of gelatin, glue, lacquers, varnishes, and casein products
- Use of acetaldehyde as a flavoring agent and additive in milk products and candies and as a preservative for food and leather

The following methods are effective in controlling worker exposures to acetaldehyde, depending on the feasibility of implementation:

- Process enclosure
- Local exhaust ventilation
- General dilution ventilation
- Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetaldehyde, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetaldehyde at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, and respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetaldehyde exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetaldehyde on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. Acetaldehyde can be detected in the blood, urine, and breath of exposed individuals. However, aldehyde concentrations in these biological specimens have not been correlated with airborne concentrations of this substance. Therefore, no biological monitoring method acceptable for routine use has yet been developed for acetaldehyde.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to acetaldehyde may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetaldehyde is determined by using a silane-treated glass tube that is packed with a 225-mg backup section and a 450-mg sampling section of pretreated XAD-2 adsorbent coated with 10% (by weight) 2-(hydroxymethyl)piperidine. Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 3 liters is collected (8-hr TWA), or they are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 0.75 liter is collected (STEL). Analysis is conducted by gas chromatography using a nitrogen/phosphorus detector. The limit of detection for this procedure is 580 parts per billion. This method is described in the OSHA Computerized Information System [OSHA 1990]. A similar method for sampling and analyzing acetaldehyde is included in Method 2538 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acetaldehyde contacts the skin, workers should immediately flush the affected areas with large amounts of water and then wash with soap and water.

Clothing and shoes contaminated with acetaldehyde should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of acetaldehyde, particularly its potential for causing skin or eye burns on prolonged contact.

A worker who handles acetaldehyde should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetaldehyde or a solution containing acetaldehyde is handled, processed, or stored.

STORAGE

Acetaldehyde should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Bulk quantities of acetaldehyde should be stored outside in detached, refrigerated tanks that conform to the requirements of the hazard communication standard. Storage in an inert gas atmosphere is recommended. Only nonsparking tools and equipment should be used to handle this OSHA Class IA flammable liquid. Containers of acetaldehyde should be protected from physical damage and should be stored separately from alkaline materials, acids, halogens, alcohols, ammonia, amines, ketones, hydrogen sulfide, hydrogen cyanide, acid anhydrides, phenols, oxidizing agents, and all ignition sources. All electrical service in storage areas should be of explosionproof design. To prevent static sparks, containers and equipment used to transfer acetaldehyde should be electrically grounded and bonded. Because empty containers may contain acetaldehyde residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetaldehyde, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete.

The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Provide maximum explosionproof ventilation to ventilate area of leak or spill.
5. Use nonsparking tools during cleanup.
6. Use water spray to flush spills away from workers and to dilute the spill.
7. Absorb small liquid spills with paper towels, vermiculite, or sand and place the material in a covered container for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the acetaldehyde for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetaldehyde is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetaldehyde is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acetaldehyde per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetaldehyde emitted or released from their facility annually.

- ***Hazardous waste management requirements***

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acetaldehyde is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U001. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acetaldehyde may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of acetaldehyde are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetaldehyde exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent skin contact with acetaldehyde. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acetaldehyde and have demonstrated good-to-excellent resistance: Teflon®, butyl rubber, and polyethylene/ethylene vinyl alcohol. Butyl rubber may provide more than 8 hr of resistance to permeation by acetaldehyde. Natural rubber, neoprene, nitrile rubber, polyethylene, polyvinyl alcohol, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by acetaldehyde.

If acetaldehyde is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Splashproof safety glasses, goggles, or face shields should be worn during operations in which there is any possibility of eye contact with acetaldehyde. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with this substance. Contact lenses should not be worn if the potential exists for acetaldehyde exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETIC ACID

INTRODUCTION

This guideline summarizes pertinent information about acetic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_2H_4O_2$

- **Structure**

CH_3COOH

- **Synonyms**

Ethanoic acid, ethylic acid, glacial acetic acid, methanecarboxylic acid, vinegar acid

- **Identifiers**

1. CAS No.: 64-19-7
2. RTECS No.: AF1225000
3. DOT UN: 2789 29 (glacial acetic acid or acetic acid solutions that are more than 80% acid); DOT UN: 2790 60 (aqueous solutions that are more than 10% but not more than 80% acid)
4. DOT labels: Corrosive, Flammable Liquid (glacial acetic acid or acetic acid solutions that are more than 80% acid); Corrosive (aqueous solutions that are more than 10% but not more than 80% acid)

- **Appearance and odor**

At temperatures above 16.7°C (62°F), acetic acid is a clear, colorless, combustible liquid with a pungent, vinegarlike odor. The odor threshold is reported to be between 0.21 and 1.0 parts per million (ppm) parts of air. This substance is available commercially in strengths ranging from 6% to more than 99% acid, by weight. Glacial acetic acid is 99.4% acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data (glacial acetic acid)**

1. Molecular weight: 60.1
2. Boiling point (at 760 mm Hg): 118°C (244.4°F)
3. Specific gravity (water = 1): 1.05 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetic acid): 2.1
5. Melting point: 16.7°C (62°F)
6. Vapor pressure at 20°C (68°F): 11 mm Hg
7. Solubility: Miscible with water, alcohol, glycerol, carbon tetrachloride, and ether; insoluble in carbon disulfide
8. Evaporation rate (butyl acetate = 1): 1.0

- **Reactivity**

1. Conditions contributing to instability: Heat and freezing temperatures. The vapor of acetic acid forms explosive mixtures with air.
2. Incompatibilities: Fires or explosions may result from contact of acetic acid with chromic acid, ammonium nitrate, sodium peroxide, nitric acid, phosphorus trichloride, or other oxidizers.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released when acetic acid is heated to decomposition.

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4. Special precautions: Acetic acid is highly corrosive in concentrated form; it corrodes metals, some coatings, and some forms of plastic and rubber.

- **Flammability (glacial acetic acid)**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to glacial acetic acid.

1. Flash point: 39°C (103°F) (closed cup). The flash point of concentrated solutions of acetic acid approaches that of glacial acetic acid; dilute acetic acid solutions are not combustible.

2. Autoignition temperature: 427°C (800°F). Dilute acetic acid solutions are not combustible.

3. Flammable limits in air (% by volume): Lower, 4.0; upper, 16.0

4. Extinguishant: Use water spray, dry chemical, alcohol foam, or carbon dioxide to fight fires involving acetic acid. Use water spray to keep fire-exposed containers cool. If a leak or spill has not ignited, water may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving acetic acid should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetic acid. Firefighters' protective clothing may not provide protection against permeation by acetic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetic acid is 10 ppm of air (25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (25 mg/m^3) as an 8-hr TWA and 15 ppm (37 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetic acid a threshold limit value (TLV) of 10 ppm (25 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 15 ppm (37 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation to the eyes, nose, and respiratory tract associated with exposure to acetic acid.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetic acid can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: Glacial acetic acid is corrosive to tissues, and concentrated acetic acid solutions (greater than 80% acid) can cause moderate to severe burns. Exposure to the vapors of acetic acid causes eye, skin, mucous membrane, and upper respiratory tract irritation.

When applied to the skin of guinea pigs, acetic acid solutions of 80% or more caused severe burns; concentrations of 50% to 80% caused moderate to severe burns; concentrations of less than 50% caused relatively minor skin damage; and solutions of 10% or less caused no injury [Proctor et al. 1988]. When glacial acetic acid was applied to the eyes of rabbits, it caused immediate and complete destruction; splashes of less concentrated solutions caused less damage [Grant 1986]. The dermal LD_{50} for rabbits was 1,060 mg/kg [NIOSH 1991]. When acetic acid was inhaled, the lowest LC_{50} for mice and guinea pigs exposed for 1 hr was approximately 5,000 ppm [NLM 1991]. Guinea pigs exposed for 1 hr to airborne acetic acid concentrations ranging from 5 to 500 ppm showed an increase in pulmonary flow resistance, a decrease in lung compliance, and an increase in the time constant of the lungs and minute volume [Amdur 1961]. At concentrations above 100 ppm, guinea pigs also showed labored breathing and a decrease in respiratory rate [Amdur 1961]. Mice exposed to acetic acid vapor at approximately

1,000 ppm showed signs of conjunctival and upper respiratory tract irritation [Clayton and Clayton 1981]. The oral LD_{50} in rats was 3,530 mg/kg [NIOSH 1991].

2. *Effects on Humans*: In vapor form, acetic acid is a severe irritant of the eyes, mucous membranes, upper respiratory tract, and skin. In contact with the skin or eyes, acetic acid solutions of 80% or more can be corrosive, causing severe burns of any exposed tissue. Long-term exposure to the vapors of this substance causes chronic bronchitis and other respiratory effects, erosion of tooth enamel, and cracking and darkening of the exposed skin.

When splashed into the eye, glacial acetic acid has caused permanent corneal opacity; skin contact with glacial acetic acid causes burns and tissue destruction [NLM 1991; AIHA 1978]. Ingestion of corrosive concentrations can cause tissue destruction, perforation, and stricture (delayed) of the throat, esophagus, and stomach; intestinal hemorrhage; and heart and renal damage [NLM 1991]. Unacclimatized individuals have experienced eye irritation at concentrations below 10 ppm, tolerable irritation at 25 ppm, and intolerable eye, nose, and throat irritation at 50 ppm [Proctor et al. 1988]. Exposure at 800 to 1,200 ppm becomes intolerable within 3 min of exposure [ACGIH 1991a]. Five workers who had been exposed to acetic acid vapor at 80 to 200 ppm for 7 to 12 years had thickening and blackening of the skin on the hands, eye inflammation, dental erosion (of both canines and incisors), and chronic pharyngitis and bronchitis [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetic acid vapor can cause redness, inflammation, lacrimation, runny nose, sore throat, coughing, bronchitis, pulmonary edema, labored breathing, and dyspnea. Death can result from circulatory collapse, renal failure, or glottic edema. Skin contact with concentrated solutions of acetic acid produces redness, blistering, and deep burns; these signs may be delayed for as long as 4 hr after contact. Eye contact with concentrated solutions of acetic acid causes immediate pain and tearing, redness, photophobia, and corneal opacities; if the exposure is severe, vision may be permanently impaired. In addition, ingestion can produce throat, esophageal, and gastric irritation, corrosion, stricture, and perforation; nausea; vomiting; diarrhea; hemorrhage; and shock.

2. *Chronic exposure*: Acetic acid vapors can cause sore throat, coughing, difficult breathing, decrements in pulmonary function, and erosion of the enamel on the incisors and canine teeth. Skin sensitization has rarely been reported. Long-term exposure of the skin to acetic acid vapor may cause it to darken, thicken, and crack.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetic acid! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetic acid are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetic acid or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures

(e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetic acid and may result in worker exposures to this substance:

—Production of cellulose acetate, vinyl acetate, inorganic acetates, organic acetates (esters), acetic anhydride, chloroacetic acid, ethyl alcohol, ketene, methyl ethyl ketone, acetone, acetanilide, and acetyl chloride

—Use of acetic acid in the dyeing, pharmaceutical, canning, fermentation, and food-preserving industries; in pigment production; and in the tanning of rubber

—Use of acetic acid as a solvent in the liquid-phase oxidation of p-xylene to terephthalic acid, as a fungicide, and as an insecticide

—Use of acetic acid in the production of plastics and photographic chemicals, as a natural latex coagulant, as an oil-well acidizer, in textile printing, as a laundry sour (neutralizer), and as a solvent for gums, resins, volatile oils, and other substances

—Use of acetic acid in the manufacture of Paris green, white lead, and rinse and stain removers

The following methods are effective in controlling worker exposures to acetic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, teeth, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with keratoconjunctivitis or other eye disorders, skin allergies or other skin disorders, erosion of tooth enamel, or respiratory disorders.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetic acid on the eyes, skin, teeth, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetic acid is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 270 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. The limit of detection for this procedure is 0.01 mg/sample. This method is an OSHA modification of Method 1603 from the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Acetic acid can be absorbed through the skin in toxic amounts, and concentrated solutions of this substance can also cause skin burns. Therefore, if acetic acid contacts the skin, workers should immediately rinse the affected areas with large amounts of water for a minimum of 15 min.

Clothing and shoes contaminated with acetic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the corrosive properties of acetic acid.

A worker who handles acetic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetic acid is handled, processed, or stored.

STORAGE

Acetic acid should be stored in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area should be detached and should be well-ventilated and have acid-resistant floors. The temperature of the storage area should be maintained above 16.7°C (62°F) to prevent rupturing of the containers. Electrical fixtures in the storage area should be vaporproof, and any tools used should be of the nonsparking type. Containers of acetic acid should be protected from physical damage and should be stored separately from oxidizing agents, combustible materials, heat, sparks, and open flame. Because empty containers may contain acetic acid residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. If the vapor from the spill has not ignited, use water spray to reduce the vapors and to protect workers attempting to stop the leak.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the acetic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- ***Respiratory protection program***

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any possibility of skin contact with acetic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by acetic acid and may provide protection for periods greater than 8 hr: butyl rubber, Teflon®, and Saranex®. Materials that may withstand permeation for more than 4 but fewer than 8 hr are neoprene, polyethylene, and polyethylene/ethylene vinyl alcohol. Natural rubber, polyvinyl chloride, and Viton® demonstrated questionable protection against permeation by acetic acid. Nitrile rubber and polyvinyl alcohol have demonstrated poor resistance to permeation by acetic acid.

If acetic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetic acid might contact the eyes (e.g., through splashes of solution). Splashproof, gas-tight goggles may also be required to prevent irritation of the eyes from acetic acid vapor. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetic acid. Contact lenses should not be worn if the potential exists for acetic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETIC ANHYDRIDE

INTRODUCTION

This guideline summarizes pertinent information about acetic anhydride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_6O_3$

- **Structure**

$(CH_3CO)_2O$

- **Synonyms**

Acetanhydride, acetic acid anhydride, acetyl ether, acetic oxide, acetyl oxide, ethanoic anhydride

- **Identifiers**

1. CAS No.: 108-24-7
2. RTECS No.: AK1925000
3. DOT UN: 1715 39
4. DOT labels: Corrosive, Flammable Liquid

- **Appearance and odor**

Acetic anhydride is a colorless liquid with a strong, pungent, vinegarlike odor. The odor threshold is reported to be between 0.13 and 0.34 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.1
2. Boiling point (at 760 mm Hg): 139°C (282°F)
3. Specific gravity (water = 1): 1.08 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetic anhydride): 3.5
5. Melting point: −73°C (−99.4°F)
6. Vapor pressure at 20°C (68.8°F): 4 mm Hg
7. Solubility: Soluble in cold water; decomposes in hot water to form acetic acid; miscible with alcohol, chloroform, ether, and ethyl acetate
8. Evaporation rate (butyl acetate = 1): 0.46

- **Reactivity**

1. Contact of acetic anhydride vapors with water or air should be avoided.
2. Incompatibilities: Fires and explosions may result from contact of acetic anhydride with water, alcohols, strong oxidizers, chromic acid, amines, or strong caustics.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon dioxide, carbon monoxide, various hydrocarbons, and acid aerosols) may be released when acetic anhydride is heated or decomposes.
4. Special precautions: Acetic anhydride attacks some coatings and some forms of plastic and rubber. It is corrosive to iron, steel, and other metals.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to acetic anhydride.

1. Flash point: 49°C (120°F) (closed cup)
2. Autoignition temperature: 316°C (600°F)
3. Flammable limits in air (% by volume): Lower, 2.7; upper, 10.3

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use carbon dioxide or dry chemical for small fires and alcohol foam for large fires. Water should be used with caution because acetic anhydride reacts with water.

Fires involving acetic anhydride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetic anhydride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Avoid directing water into containers of acetic anhydride. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetic anhydride. Chemical protective clothing that is specifically recommended for acetic anhydride may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetic anhydride.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetic anhydride is 5 ppm (20 mg/m^3) as a ceiling limit which should not be exceeded during any part of the workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (20 mg/m^3) as a ceiling limit [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetic anhydride a ceiling limit value of 5 ppm (21 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1991a].

• Rationale for limits

The limits are based on the risk of ocular and respiratory irritation associated with high short-term exposure to acetic anhydride.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acetic anhydride can occur through inhalation, ingestion, and eye or skin contact. Acetic anhydride also penetrates the skin.

• Summary of toxicology

1. *Effects on Animals*: Acetic anhydride is highly corrosive and causes severe irritation and burns of the eyes, mucous membranes, and skin of exposed animals. When instilled into the eyes, acetic anhydride can be corrosive. It can also penetrate the intact corneal epithelium in concentrations sufficiently high to cause iritis [NLM 1992]. Guinea pigs repeatedly challenged with dermal applications of acetic anhydride developed skin sensitization [Proctor et al. 1988]. The dermal LD_{50} for rabbits is 4,000 mg/kg [NIOSH 1991]. Rats survived exposure to saturated vapors for 5 min [Deichmann and Gerade 1969]. Six rats exposed to 1,000 ppm of acetic anhydride for 4 hr survived, but those inhaling 2,000 ppm for the same interval died [ACGIH 1991b]. The oral LD_{50} for rats is 1,780 mg/kg.

2. *Effects on Humans*: Exposure to acetic anhydride in either the liquid or vapor form causes severe irritation of the eyes, skin, and mucous membranes in humans. Eye contact can lead to corneal burns, erosion, edema, scarring, cataracts with temporary or permanent visual impairment, and inflammation and structural damage of the iris [Grant 1986; Klaassen et al.1986]. In contact with the skin, acetic anhydride causes delayed burns that may be slow to heal [Grayson 1985; Sittig 1985]. The vapor of this substance is reported to be irritating even at a concentration as low as 0.09 ppm [NLM 1992]. Workers exposed to concentrations of acetic anhydride greater than 5 ppm experienced acute eye and upper respiratory tract irritation; their symptoms included severe eye pain and difficult breathing [Proctor et al. 1988]. Inhalation of high concentrations of this substance can cause bronchospasm and ulceration of the nasal mucosa [Proctor et al. 1988]. Humans exposed to the vapor of acetic anhydride occasionally become sensitized to this substance [Proctor et al. 1988]. Ingestion of acetic anhydride can cause corrosion of oral, esophageal, and gastric tissues as well as hemorrhages, strictures, and stenoses but rarely perforations [NLM 1992].

• Signs and symptoms of exposure

1. *Acute exposure*: Acetic anhydride is corrosive to tissues. It can cause a burning sensation in the nose and throat, cough, pain in the chest, difficult breathing, dyspnea, and pulmonary edema. Exposure of the eye to liquid or vaporous acetic anhydride results in excessive tearing, redness, pain, and photophobia. In contact with the skin, acetic anhydride can cause corrosion, burns, and blisters. Ingestion can also induce clammy skin, weak and rapid pulse, nausea, vomiting,

shallow respiration, and decreased urine output. In cases where circulatory collapse has occurred and gone uncorrected for several hours, renal failure and ischemic liver and heart lesions have resulted. Death following ingestion can result from glottic edema or circulatory shock.

2. *Chronic exposure*: Acetic anhydride can cause conjunctivitis, pulmonary edema with coughing and difficult breathing, and skin sensitization with redness, itching, and wheals.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of acetic anhydride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetic anhydride are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetic anhydride or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. *Drinking a carbonated beverage or more than one cup of fluid* could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetic anhydride and may result in worker exposures to this substance:

—Manufacture of acetyl compounds, cellulose acetate, cellulose esters, chloroacetic acid, acetyl chloride, triacetate fibers, and vinyl acetate

—Processing of dyes, perfumes, explosives, and flavorings

—Electropolishing of metals and processing of semiconductors

—Use of acetic anhydride as an acetylizer and solvent in examining wool fat, glycerol, fatty and volatile oils, and resins, and in detecting rosins

—Use of acetic anhydride as a dehydrating agent in nitrations, sulfonations, and other reactions where removal of water is necessary

—Use of acetic anhydride in the manufacture of pharmaceuticals, including aspirin, and as an intermediate in the synthesis of pesticides

—Use of acetic anhydride as an esterifying agent for food starch

The following methods are effective in controlling worker exposures to acetic anhydride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations must be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetic anhydride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetic anhydride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetic anhydride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetic anhydride on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetic anhydride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetic anhydride is determined by using a standard midget bubbler containing 10 ml of alkaline hydroxylamine hydrochloride solution. The absorbing solution is made up of equal volumes of hydroxylamine hydrochloride (200 g in 1 liter distilled water) and sodium hydroxide (200 g in 1 liter distilled water). The solution is mixed just before use and is stable for only 2 hr. Samples are collected at a recommended flow rate of 0.2 to 1 liter/min until a recommended air volume of 25 to 100 liters is collected. Analysis is performed colorimetrically using visible absorption spectrophotometry. A purple-colored complex is formed by adding ferric chloride solution to the sample. The limit of detection for this procedure is 0.05 mg/sample. This method is described in Method 3506 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acetic anhydride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water. Get medical help immediately.

Clothing and shoes contaminated with acetic anhydride should be removed immediately and provisions should be made for safely removing this chemical from these articles. If gross exposure occurs, remove contaminated clothing under a safety shower. Speed in removing the contaminated material from the skin is extremely important. Persons laundering contaminated clothing should be informed about the hazardous properties of acetic anhydride, particularly its potential to be corrosive to the skin.

A worker who handles acetic anhydride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetic anhydride or a solution containing acetic anhydride is handled, processed, or stored.

STORAGE

Acetic anhydride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Inside storage must be in a standard flammable liquids storage room or cabinet. Steel, galvanized tin, tinned iron, copper, or copper alloys should not be used for piping or valves that will be in contact with acetic anhydride. Containers of acetic anhydride should be protected from physical damage and should be separated from water, alcohols, strong oxidizers, chromic acid, amines, strong caustics, heat, sparks, and open flame. Because containers that formerly contained acetic anhydride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetic anhydride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. If the leak or spill has not ignited, water spray may be used to reduce vapors.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal. Wash the site with soda ash solution and flush with plenty of water.
7. For large liquid spills, build dikes far ahead of the spill to contain the acetic anhydride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetic anhydride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acetic anhydride is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetic anhydride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetic anhydride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetic anhydride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with acetic anhydride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acetic anhydride and have demonstrated protection for more than 4 but fewer than 8 hr: butyl rubber and Teflon®. Polyvinyl chloride, nitrile rubber, Viton®, and natural rubber have all demonstrated poor resistance to permeation by acetic anhydride.

If acetic anhydride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetic anhydride might contact the eyes (e.g., through vapors or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetic anhydride. Contact lenses should not be worn if the potential exists for acetic anhydride exposure.

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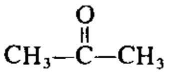
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETONE

INTRODUCTION

This guideline summarizes pertinent information about acetone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_3H_6O
- **Structure:**



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

- **Synonyms:** Dimethyl ketone, ketone propane, propanone, 2-propanone
- **Identifiers:** CAS 67-64-1; RTECS AL3150000; DOT 1090, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a fragrant, mintlike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58.09
2. Boiling point (at 760 mmHg): 56.2 °C (133 °F)
3. Specific gravity (water = 1): 0.79
4. Vapor density (air = 1 at boiling point of acetone): 2.0
5. Melting point: -94.8 °C (-138 °F)
6. Vapor pressure at 20 °C (68 °F): 180.0 mmHg; at 25 °C (77 °F), 226.3 mmHg
7. Miscible in water
8. Evaporation rate (butyl acetate = 1): 6
9. Saturation concentration in air (approximate) at 20 °C (68 °F): 23.7% (237,000 ppm); at 25 °C (77 °F), 29.8% (298,000 ppm)
10. Ionization potential: 9.69 eV

- **Reactivity**

1. Incompatibilities: Contact with acids and oxidizing materials may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., ketene) may be released in a fire involving acetone.
3. Caution: Acetone will dissolve most plastics, resins, and rubber.

- **Flammability**

1. Flash point: -18.0 °C (0 °F) (closed cup)
2. Autoignition temperature: 465 °C (869 °F)
3. Flammable limits in air, % by volume: Lower, 2.2; Upper, 13
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 20 ppm
2. Eye irritation levels: Acetone has been reported to cause a burning sensation of the eyes at a vapor concentration of 500 ppm. Other reports have concluded that irritation in acclimated workers occurs between 1,000 and 1,500 ppm.
3. Evaluation of warning properties for respirator selection: Because of its odor, acetone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetone is 1,000 parts of acetone per million parts of air (ppm) [2,400 milligrams of acetone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 250 ppm (590 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 750 ppm (1,780 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek; the (ACGIH) short-term exposure limit (STEL) is 1,000 ppm (2,375 mg/m^3) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for acetone

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	1,000	2,400
NIOSH REL TWA	250	590
ACGIH TLV® TWA	750	1,780
STEL	1,000	2,375

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Acetone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of acetone produced depression of respiration and narcosis in rats. Subchronic dermal application or subcutaneous injection of acetone produced cataracts in guinea pigs.
2. *Effects on humans:* Acute inhalation of acetone has produced narcosis, and repeated exposures have caused inflammation of the respiratory tract, stomach, and small intestine. Studies of persons clinically exposed indicate that acetone is metabolized slowly and may accumulate in the body throughout a 40-hour workweek.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to acetone can cause eye irritation, dryness of the mouth and throat, nausea, vomiting, headache, sleepiness, dizziness, light-headedness, weakness, incoordination, loss of energy, fainting, and unconsciousness.
2. *Long-term (chronic):* Exposure to acetone can cause dizziness and sleepiness. Dryness, irritation, and inflammation of skin can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to acetone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to acetone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to acetone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to acetone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting acetone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure acetone may also be used if available. A detailed sampling and analytical method for acetone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with acetone.

Workers should be provided with and required to use splash-proof safety goggles where acetone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with acetone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of acetone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of acetone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with acetone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle acetone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to acetone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for acetone

Operations	Controls
During application of lacquer, paints, and varnishes	Natural ventilation, local exhaust ventilation, workroom ventilation, personal protective equipment
During use of solvents and cementing agents	Personal protective equipment
During dip application of protective coatings; during cleaning operations	Local exhaust ventilation, personal protective equipment
During fabric coating and dyeing processes	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to acetone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If acetone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to acetone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If acetone gets on the skin, wash it immediately with soap and water. If acetone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. If irritation persists after washing, get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

In cases in which environmental levels exceed the NIOSH REL, workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If acetone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing acetone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from acetone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing acetone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Acetone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing acetone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for acetone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s)
	Any powered air-purifying respirator with organic vapor cartridge(s)
	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 6,250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 12,500 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
Less than or equal to 20,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 20,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 250 ppm (590 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETONITRILE

INTRODUCTION

This guideline summarizes pertinent information about acetonitrile for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_2H_3N

- **Structure**

CH_3CN

- **Synonyms**

Methyl cyanide, cyanomethane, ethanenitrile, ethyl nitrile, methanecarbonitrile

- **Identifiers**

1. CAS No.: 75-05-8
2. RTECS No.: AL7700000
3. DOT UN: 1648 28
4. DOT labels: Flammable Liquid and Poison

- **Appearance and odor**

Acetonitrile is a flammable, colorless liquid with an aromatic odor. The odor threshold is reported to be 40 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 41
2. Boiling point (at 760 mm Hg): 81.6°C (178.9°F)
3. Specific gravity (water = 1): 0.79 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetonitrile): 1.42
5. Melting point: −45°C (−49°F)
6. Vapor pressure at 20°C (68°F): 73 mm Hg
7. Solubility: Miscible with water, methanol, methyl acetate, ethyl acetate, alcohol, ethanol, acetone, acetamide solutions, carbon tetrachloride, chloroform, ethylene chloride, and many unsaturated hydrocarbons
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame. Vapors form explosive mixtures with air.
2. Incompatibilities: Fire and explosion may result from contact of acetonitrile with perchloric acid, iron (III) salts of perchlorate, nitric acid, oleum, indium, nitrating agents, perfluorourea, chlorosulfonic acid, or other strong oxidizers.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen, carbon monoxide, carbon dioxide, and hydrogen cyanide) may be released in a fire involving acetonitrile.
4. Special precautions: Liquid acetonitrile attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to acetonitrile.

1. Flash point: 5.6°C (42°F) (closed cup)
2. Autoignition temperature: 523.9°C (975°F)
3. Flammable limits in air (% by volume): Lower, 4.4; upper, 16.0

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

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Occupational Safety and Health Administration

4. Extinguishant: Use carbon dioxide, dry chemical, or foams on fires involving acetonitrile. Never direct a stream of water into burning pools of liquid acetonitrile because this may scatter and spread the flames. Water spray may be used to cool containers or to protect persons attempting to stop the leak.

Fires involving acetonitrile should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetonitrile may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetonitrile. Chemical protective clothing that is specifically recommended for acetonitrile may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetonitrile.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetonitrile is 40 ppm (70 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 60 ppm (105 mg/m^3) as a short-term exposure limit (STEL) [29 CFR 1910.1000, Table Z-1-A]. A STEL is a 15-min TWA exposure that should not be exceeded at any time during the workday.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 20 ppm (34 mg/m^3) as a TWA for up to a 10-hr workshift and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetonitrile a threshold limit value (TLV) of 40 ppm (67 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 60 ppm (101 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risks of organic cyanide poisoning and liver and respiratory tract injuries associated with exposure to acetonitrile.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetonitrile can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Acetonitrile can induce methemoglobinemia and cyanosis because it is metabolized in the body to cyanide. The 8-hr LC_{50} in rats is 7,500 ppm [NIOSH 1991]. The dermal LD_{50} in rabbits is 1,250 mg/kg [NIOSH 1991]. Acutely poisoned animals convulsed and became prostrate before death; autopsy of these animals revealed pulmonary hemorrhage [Proctor et al. 1988]. In mice exposed to 200 or 400 ppm for 6.5 hr/day, 5 days/week for 13 weeks, an increase in liver weight and pathological changes in liver cells were seen at autopsy; signs of anemia were also seen in the high-dose groups before death [ACGIH 1991a]. Dogs and monkeys exposed to a 350-ppm concentration for 7 hr/day, 3 days/week for 13 weeks showed signs of emphysema and other reactive changes in the lungs at autopsy; the monkeys also exhibited brain hemorrhage [Clayton and Clayton 1982]. The oral LD_{50} in rats is 2,730 mg/kg. Teratogenic and embryotoxic effects occurred in hamsters inhaling 5,000 or 8,000 ppm for 1 hr on day 8 of gestation, and a single oral or intraperitoneal dose of 100 to 400 mg/kg also resulted in teratogenic effects in the offspring of exposed rats [ACGIH 1991a].

2. *Effects on Humans*: Acetonitrile is a primary irritant of the eyes, mucous membranes, skin, and upper respiratory tract of exposed workers; it has also caused methemoglobinemia and death in humans acutely overexposed. Two volunteers experienced no ill effects after inhaling 80 ppm for 4 hr; however, one of these individuals experienced bronchial irritation after an exposure to 160 ppm for the same interval [Proctor et al. 1988]. Ten painters developed signs of systemic toxicity when exposed to the vapor of a mixture containing 30% to 40% acetonitrile for 2 workdays. Four of the ten printers required hospitalization. One painter died after experiencing massive hematemesis [Proctor et al. 1988]. Several other industrial fatalities have occurred as a result of acute overexposure to acetonitrile. The lowest oral dose toxic in humans is 570 mg/kg; ingestion of this amount of acetonitrile caused gastrointestinal tract disturbances [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acetonitrile poisoning can cause flushing or ashen-grey color; chest tightness; headache; nausea; vomiting (with or without blood); sweating; excess saliva production; lassitude; muscle weakness; painful, difficult, or irregular breathing; convulsions; stupor; coma; and cardiac and respiratory arrest.

2. *Chronic exposure*: No signs or symptoms of chronic exposure have been reported.

- **Emergency procedures**

[illegible]

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetonitrile. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetonitrile are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Do ***not*** induce vomiting.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acetonitrile may result in worker exposures to this substance:

—Use as a solvent for extractive distillation in the manufacture of butadiene and isoprene

—Use as an extractive solvent in separation of fatty acids from fish liver oils; to remove phenol, tar, and color from petroleum hydrocarbons; to recover various alcohols, acids, and dark wood rosins; and in chemical analysis

—Use as a solvent and reactive medium for the preparation of pharmaceuticals, waterproofing compounds, antistatic agents, detergents, polymers, dyestuff intermediates, and for chemical research

—Use as an indifferent medium in physiochemical investigation and in separation of alkaloids in tissue extraction

—Use as a solvent for recrystallization and purification of salts, metals, and steroids; as a spinning solvent for synthetic fibers; as a solvent for epoxy resin coatings

—Use in organic synthesis in preparation of vitamins, perfumes, water softeners, and plasticizers, and as a catalyst to promote ionization reactions

The following methods are effective in controlling worker exposures to acetonitrile, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations must be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetonitrile, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and kidneys and of the cardiovascular, respiratory, and central nervous systems. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetonitrile at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with liver, kidney, cardiovascular, respiratory, or central nervous system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetonitrile exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetonitrile on the liver, kidneys, and cardiovascular, respiratory, and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Acetonitrile exposure can be monitored by measurement of its metabolites, cyanide and thiocyanate, in the blood or in plasma and urine, respectively. Some sources suggest that blood cyanide levels of 0.1 mg/l or plasma or urine thiocyanate levels above 20 mg/l indicate excessive exposure. Because smokers often have higher levels of both metabolites, pre-exposure baseline measurements are suggested to establish each worker's baseline level.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetonitrile is determined by using coconut shell charcoal tubes (400/200-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 25 liters is collected. The sample is then treated with benzene to extract the acetonitrile. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 1606 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Clothing and shoes contaminated with acetonitrile should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Work clothing should not be taken home for laundering. Persons laundering contaminated clothing should be informed about the hazardous properties of acetonitrile, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles acetonitrile should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetonitrile or a solution containing this substance is handled, processed, or stored.

STORAGE

Acetonitrile should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage must be in a standard flammable liquids storage area. All electrical service in the storage area should meet code requirements for flammable atmospheres. Containers of acetonitrile should be protected from physical damage and should be stored separately from perchloric acid, iron (III) salts of perchlorate, nitric acid, oleum, indium, nitrating agents, perfluorourea, chlorosulfonic acid, other strong oxidizers, heat, sparks, and open flame. To prevent static sparks, conveying equipment and storage containers should be electrically grounded and bonded during transfer. Because containers that formerly contained acetonitrile may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetonitrile, persons not wearing protective equipment and clothing should be restricted from contaminated areas until the cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Isolate and ventilate the area of the spill or leak.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered, vapor-tight container for later disposal.
6. Large quantities of acetonitrile can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetonitrile is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetonitrile is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at *(800) 424-8802 or at (202) 426-2675 in Washington, D.C.* [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of this substance per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetonitrile emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acetonitrile is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U003. This substance has been banned from land disposal and may be treated by incineration. Acetonitrile also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetonitrile exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves, boots, aprons, and gauntlets should be worn as necessary to prevent skin contact either with the vapor or the liquid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acetonitrile and have demonstrated good-to-excellent resistance for periods of at least 8 hr: butyl rubber, polyvinyl alcohol, and Teflon®. Natural rubber, neoprene, nitrile, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation.

If acetonitrile is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetonitrile might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetonitrile. Contact lenses should not be worn if the potential exists for acetonitrile exposure.

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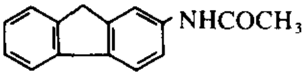
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
2-ACETYLAMINOFLUORENE
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 2-acetylaminofluorene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{15}H_{13}NO$
- **Structure:**



- **Synonyms:** 2-AAF; 2-acetamidofluorene; 2-acetaminofluorene; N-acetyl-2-aminofluorene; 2-(acetylamino)fluorene; N-FAA; 2-FAA
- **Identifiers:** CAS 53-96-3; RTECS AB9450000; DOT not assigned
- **Appearance:** Tan, crystalline solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 223.29
2. Melting point: 194°C (381.2°F)
3. Insoluble in water

- **Flammability**

Extinguishant: Dry chemical, carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 2-acetylaminofluorene; however, the OSHA standard requires implementation of stringent controls wherever 2-acetylaminofluorene or solid or liquid mixtures containing at least 0.1% by weight or volume of 2-acetylaminofluorene are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1014, 2-Acetylaminofluorene. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have an assigned threshold limit value (TLV®) for 2-acetylaminofluorene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Acetylaminofluorene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Subchronic or chronic oral administration of 2-acetylaminofluorene in dogs, rats, or hamsters produced cancers of the bladder or liver. In rats, cancers of the kidneys, pancreas, pelvis, salivary glands, eyes, ear ducts, and auditory and sebaceous glands were also found. In all animals that developed cancer from exposure to 2-acetylaminofluorene, the potent carcinogenic metabolite N-hydroxy-2-acetylaminofluorene was produced. Single oral doses of 2-acetylaminofluorene to pregnant rats on days 8-12 of gestation induced fetal malformations (hydrocephaly).
2. *Effects on humans:* Five cancer patients treated with single oral doses of 2-acetylaminofluorene produced the N-hydroxy-2-acetylaminofluorene metabolite, indicating that 2-acetylaminofluorene may be metabolized in humans as it was in animals that developed cancer from exposure to 2-acetylaminofluorene.

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Division of Standards Development and Technology Transfer

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to 2-acetylaminofluorene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, urinary tract, and reproductive system.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-acetylaminofluorene. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-acetylaminofluorene. Because the metabolite N-hydroxy-2-acetylaminofluorene has been identified in both animals and humans administered 2-acetylaminofluorene, consideration should be given to monitoring for this metabolite in workers who may be exposed to 2-acetylaminofluorene.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 2-acetylaminofluorene may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• Method

There is no NIOSH-validated sampling or analytical method for 2-acetylaminofluorene.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory type hoods" or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system. If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 2-acetylaminofluorene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 2-acetylaminofluorene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-acetylaminofluorene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 2-acetylaminofluorene from materials and equipment. Contaminated materials should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1014:

Areas where 2-acetylaminofluorene is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 2-acetylaminofluorene, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 2-acetylaminofluorene which are not in an isolated system, laboratory type hood, or other system affording equivalent protection against the entry of 2-acetylaminofluorene into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory type hoods" or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 2-acetylaminofluorene shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 2-acetylaminofluorene from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-acetylaminofluorene may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 2-acetylaminofluorene

Operation	Controls
During use in research and labortatory facilities	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 2-acetylaminofluorene, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-acetylaminofluorene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-acetylaminofluorene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-acetylaminofluorene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use. If 2-acetylaminofluorene gets on the skin, wash it immediately with soap and water. If 2-acetylaminofluorene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 2-acetylaminofluorene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 2-acetylaminofluorene may be collected and placed in an appropriate container.
3. For small quantities of liquids containing 2-acetylaminofluorene, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing 2-acetylaminofluorene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. 2-acetylaminofluorene dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container. Dry sweeping and dry mopping of 2-acetylaminofluorene are prohibited by OSHA.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 2-acetylaminofluorene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETYLENE TETRABROMIDE

INTRODUCTION

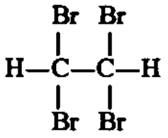
This guideline summarizes pertinent information about acetylene tetrabromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CHBr_2CHBr_2$

- **Structure**



$$H-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-H$$

- **Synonyms**

Tetrabromacetylene, tetrabromoethane; symmetrical tetrabromoethane; 1,1,2,2-tetrabromoethane (TBE); Muthmann's liquid

- **Identifiers**

1. CAS No.: 79-27-6
2. RTECS No.: KI8225000
3. DOT UN: 2504 58
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Acetylene tetrabromide is a noncombustible, heavy, pale yellow liquid with a pungent, camphorlike odor. No quantitative data is available on the odor threshold.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 345.7
2. Boiling point (at 760 mm Hg): 239°C (462.2°F)
3. Specific gravity (water = 1): 2.96 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetylene tetrabromide): 11.9
5. Melting point: 0°C (32°F)
6. Vapor pressure at 20°C (68°F): 0.02 mm Hg
7. Solubility: Insoluble in water; miscible with alcohol, chloroform, ether, aniline, glacial acetic acid; soluble in acetone and benzene.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Toxic vapors may result from contact with chemically active metals or strong caustics, or with hot iron, aluminum, or zinc in the presence of steam.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, carbonyl bromide, brominated solvents, and carbon monoxide) may be released when acetylene tetrabromide decomposes.
4. Special precautions: Acetylene tetrabromide softens or destroys most plastics and rubbers.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to acetylene tetrabromide; this substance is not combustible.

1. Flash point: −18°C (0°F) (closed cup)
2. Autoignition temperature: 335°C (635°F)
3. Flammable limits in air: Not applicable

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4. Extinguishant: Use water to cool containers of acetylene tetrabromide that are involved in a fire.

Fires involving acetylene tetrabromide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetylene tetrabromide. Chemical protective clothing that is specifically recommended for acetylene tetrabromide may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetylene tetrabromide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetylene tetrabromide is 1 ppm (14 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for acetylene tetrabromide [NIOSH 1988, 1991].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetylene tetrabromide a threshold limit value (TLV) of 1 ppm (15 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of hepatotoxic effects associated with exposure to acetylene tetrabromide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetylene tetrabromide can occur through inhalation of the vapors, ingestion of the liquid, and eye or skin contact with the liquid or vapors.

- **Summary of toxicology**

1. *Effects on Animals*: Acetylene tetrabromide is a central nervous system depressant and a liver, kidney, and lung toxin in animals. When instilled into the eyes of rabbits, the liquid caused slight conjunctival and superficial corneal injury; on the skin of rabbits, a 24-hr application of 500 mg caused a moderate degree of irritation [NIOSH 1991]. The dermal LD_{50} in rats is 5,250 mg/kg [NIOSH 1991]. The inhalation LC_{50} in rats has been reported as 39 ppm (549 mg/m^3) [NIOSH 1991]. Although no noteworthy effects were described for rats, rabbits, and guinea pigs exposed to saturated vapors (unquantified) for up to 2 hr, 3-hr exposures produced respiratory tract irritation, tremors, and CNS depression (ataxia, loss of the righting reflex, and unconsciousness). Only the guinea pigs died, each having postmortem fatty degeneration of the hepatic and renal parenchyma. The tissues for all survivors from the four species appeared histologically normal [Gray 1950]. Female rats exposed to saturated vapors (~14 ppm at 23°C) for 7 hr did not die and had very slight eye and nasal irritation [Hollingsworth et al. 1963]. The oral LD_{50} in rats is 1,100 mg/kg [NIOSH 1991]. In a subchronic study, rats, rabbits, mice, and a monkey were exposed to ambient concentrations of 1, 4, or 14 ppm for 7 hr/day, 5 days/week for approximately 28, 26, or 15 weeks, respectively. The no observable effect level (NOEL) was 1 ppm. The 4-ppm concentration induced slight lung hemorrhage, congestion, edema, slight hepatocellular centrolobular fatty degeneration, and slight swelling of the renal convoluted tubules. Similar pulmonary and liver changes were reported at 14 ppm [Hollingsworth 1963]. Application of 15 mg to the skin of mice, followed 14 days later with a tumor-promoting agent (phorbol myristate acetate) caused a statistically significant increase in forestomach papillomas [Van Duuren et al. 1979; Proctor et al. 1988; NLM 1991].

2. *Effects on Humans*: Acetylene tetrabromide is a central nervous system depressant and a liver toxin in humans. When a chemist was exposed to this substance for 7.5 hr at an estimated concentration of 1 to 2 ppm with a single 10-min peak exposure to 16 ppm, he experienced headache, anorexia, nausea, vomiting, and abdominal pain. During a 9-week hospitalization, clinical studies revealed icterus, urobilinuria, bilirubinuria, and severe and nearly fatal liver damage [Proctor et al. 1988; Clayton and Clayton 1981]. Skin absorption of acetylene tetrabromide may also have been involved in this episode of acute poisoning [Proctor et al. 1988; ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetylene tetrabromide can cause irritation of the eyes, nose, and upper respiratory tract; headache; nausea; vomiting; anorexia; abdominal pain; ataxia; CNS depression; and death. Jaundice, urobilinuria, bilirubinuria, and monocytosis have also been reported. Exposure to the eyes or skin with liquid acetylene tetrabromide may cause pain, redness, and a slight but reversible conjunctival irritation and corneal injury.

2. *Chronic exposure*: On the basis of effects seen in animals, exposure to acetylene tetrabromide can cause liver, kidney, and lung damage.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetylene tetrabromide. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetylene tetrabromide are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose to remove residues from nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetylene tetrabromide or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acetylene tetrabromide may result in worker exposures to this substance:

—Use as a catalyst or catalytic initiator in manufacture of terephthalic acid and synthetic fibers and as a polymer additive in flameproof, flame-retardant polystyrenes, polyurethanes, and polyolefins

—Use in the density separation of mineral salts

—Use as a mercury substitute in gauges, as a level indicator in sight gauges, and as a refractive index liquid in microscopy

—Use as a solvent for fats, oils, and waxes

—Use as an ore flotation agent

The following methods are effective in controlling worker exposures to acetylene tetrabromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers

for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetylene tetrabromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetylene tetrabromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with impaired liver function.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetylene tetrabromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetylene tetrabromide on the eyes, skin, upper respiratory tract, liver, and kidneys. Liver function studies should be performed on a routine basis, particularly in workers exposed to acetylene tetrabromide levels near the PEL. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetylene tetrabromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetylene tetrabromide is determined by using a silica gel absorption tube (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. The sample is then treated with tetrahydrofuran to extract the acetylene tetrabromide. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.16. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 2003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acetylene tetrabromide contacts the skin, workers should immediately wash the affected areas thoroughly with soap and water.

Clothing and shoes contaminated with acetylene tetrabromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of acetylene tetrabromide.

A worker who handles acetylene tetrabromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetylene tetrabromide is handled, processed, or stored.

STORAGE

Acetylene tetrabromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of acetylene tetrabromide should be protected from physical damage and should be stored separately from chemically active metals and strong caustics, heat, sparks, and open flame. Because empty containers may contain acetylene tetrabromide residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetylene tetrabromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. If feasible, remove leaking containers to a safe place.
4. Ventilate atmosphere to reduce vapors.
5. Absorb small spills with sand, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the acetylene tetrabromide for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetylene tetrabromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center about an accidental release of acetylene tetrabromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the annual amount of acetylene tetrabromide emitted or released from their facility.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetylene tetrabromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetylene tetrabromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with acetylene tetrabromide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Such clothing may include gloves with long sleeves, aprons, footwear, and face shields. No reports have been published on the resistance of various protective clothing materials to permeation by acetylene tetrabromide; however, Viton®, Teflon®, and polyvinyl alcohol materials have been tested against permeation by a similar compound (ethylene dibromide) and have been found to provide good-to-excellent protection. These materials provided more than 8 hr of resistance to permeation by ethylene dibromide. Since specific test data are not available for acetylene tetrabromide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to acetylene tetrabromide.

If acetylene tetrabromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Chemical safety glasses, goggles, or face shields should be worn during operations in which acetylene tetrabromide might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetylene tetrabromide. Contact lenses should not be worn if the potential exists for acetylene tetrabromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETYLSALICYLIC ACID

INTRODUCTION

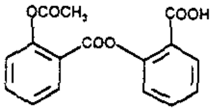
This guideline summarizes pertinent information about acetylsalicylic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CH_3COOC_6H_4COOH$

- **Structure**



- **Synonyms**

Aspirin, ASA, acetol, salicylic acid acetate, 2-acetoxybenzoic acid, acetophen, acetosalic acid, acetal, acetylin, acetylsal, acidum acetylsalicylicum, Asagran, Aspirdrops, Entericin, Caprin, Colfarit, Duramax, Empirin, Measurin, Novid, Rhodine, Saletin, Solpyron

- **Identifiers**

1. CAS No.: 50-78-2
2. RTECS No.: VO0700000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Acetylsalicylic acid is a noncombustible, crystalline, colorless to white powder. This substance is odorless; on contact with moisture, it develops the vinegarlike odor of acetic acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 180.2
2. Boiling point (at 760 mm Hg): 140°C (284°F) (decomposes)
3. Specific gravity (water = 1): 1.4 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 135°C (275°F)
6. Vapor pressure at 20°C (68°F): Negligible
7. Solubility: Soluble in water, alcohol, chloroform, and ether; less soluble in absolute ether
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires or explosions may result from contact of acetylsalicylic acid with strong oxidizers. Contact with alkali hydroxides or carbonates may cause decomposition.
3. Hazardous decomposition products: When heated to decomposition, toxic vapors and gases (such as partially oxidized hydrocarbons, carbon monoxide, and carbon dioxide) may be released.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to acetylsalicylic acid; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Acetylsalicylic acid will not burn. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Dispersed in air, the dust of acetylsalicylic acid is a serious explosion hazard. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires resulting from acetylsalicylic acid explosions.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetylsalicylic acid is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for acetylsalicylic acid of 5 mg/m^3 as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetylsalicylic acid a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of respiratory and gastric irritation associated with exposure to acetylsalicylic acid.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetylsalicylic acid can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Acetylsalicylic acid can damage the stomach lining and interfere with blood clotting; it is also fetotoxic and teratogenic in animals [Klaassen et al. 1986; NIOSH 1991]. Cats were orally administered total daily doses of either 33 to 63 mg/kg or 81 to 130 mg/kg for up to 35 days. The lowest dose induced toxic hepatitis in the treated animals, but both doses induced anorexia, weight loss, vomiting, depression, and death. Only animals receiving the high doses had hyperpnea (increased rate and depth of breathing), hyperthermia, and disturbances in their acid-base balance [NLM 1991]. Dogs administered oral daily doses of 100 to 300 mg/kg for 1 to 4 weeks vomited bloody emesis and had gastritis and gastric perforations [NLM 1991]. The oral LD_{50} in rats ranges from 1,360 to 1,750 mg/kg [NLM 1991]. Acetylsalicylic acid has been shown to be a developmental toxin in five species of animals; this substance also causes reproductive effects in both males and females [NIOSH 1991]. Teratogenic effects occurred when 125 mg/kg acetylsalicylic acid was administered orally to rats on day 12 of pregnancy; damage to the testes, epididymis, and sperm duct was observed in male rats dosed orally with 2.1 g/kg acetylsalicylic acid for 14 days [NIOSH 1991]. When administered orally or subcutaneously to pregnant rats, mice, rabbits, cats, and dogs, acetylsalicylic acid was fetotoxic or teratogenic [NIOSH 1991]. Chronic administration of a 300-mg/kg dose of acetylsalicylic acid inhibited ovulation in rats by depressing prostaglandin synthesis [NLM 1991].

2. *Effects on Humans*: In the occupational environment, acetylsalicylic acid is a systemic allergen and an irritant of the eyes, mucous membranes, upper respiratory tract, and skin. When in contact with the eyes, this substance causes irritation, conjunctival ulceration, and corneal injury [ACGIH 1991a; Grant 1986]. Aspirin-intolerant individuals develop hives, rhinorrhea, and bronchospasm when exposed to this substance; some persons (e.g., those who are glucose-6-phosphate dehydrogenase deficient) may be especially sensitive to aspirin's effects [Klaassen et al. 1986; Gosselin et al. 1984]. Ingestion of acetylsalicylic acid causes an increased tendency to bleed by interfering with platelet aggregation; this effect has been seen after the ingestion of as little as 150 mg of acetylsalicylic acid [ACGIH 1991a]. Acetylsalicylic acid produces an allergy-like response in about 0.2% of individuals; although aspirin intolerance mimics a true allergic response, this reaction is not believed to be immunologically based [Klaassen et al. 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetylsalicylic acid can cause redness and tearing of the eyes, runny nose, scratchy throat, and redness and swelling of the skin.

2. *Chronic exposure*: Chronic exposure to acetylsalicylic acid can cause headache, dizziness, and ringing in the ears; in aspirin-intolerant individuals, it can induce pseudoallergic responses (hives, runny nose, wheezing, and difficult breathing) and a permanent intolerance to this substance. Ingestion of aspirin may lead to an increase in clotting time.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. Wash contaminated skin with soap and water.

3. *Inhalation exposure*: If a large amount of acetylsalicylic acid is inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if a large amount of acetylsalicylic acid is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The manufacture, handling, and packaging of aspirin tablets or related pharmaceutical products may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to acetylsalicylic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetylsalicylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and upper respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetylsalicylic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with drug allergies or aspirin intolerance or of diseases of the eyes, skin, or upper respiratory system; individuals using anticoagulant medications may also be at increased risk.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetylsalicylic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetylsalicylic acid on the eyes, skin, or upper respiratory tract or on blood clotting time. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetylsalicylic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetylsalicylic acid is determined by using a 37-mm glass fiber filter. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If acetylsalicylic acid contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with acetylsalicylic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles acetylsalicylic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetylsalicylic acid or a solution containing acetylsalicylic acid is handled, processed, or stored.

STORAGE

Acetylsalicylic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of acetylsalicylic acid should be protected from physical damage and should be stored separately from strong oxidizers, alkali hydroxides, carbonates, moisture, and heat. Because containers that formerly contained acetylsalicylic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetylsalicylic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Collect spilled material in the most convenient and safe manner and place the material in a covered container for reclamation or later disposal in an approved facility.

2. Absorb liquid containing acetylsalicylic acid in vermiculite, dry sand, earth, or similar material.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetylsalicylic acid is not subject to EPA emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of acetylsalicylic acid; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetylsalicylic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetylsalicylic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetylsalicylic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with acetylsalicylic acid; protective gloves are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to acetylsalicylic acid permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to acetylsalicylic acid.

If acetylsalicylic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetylsalicylic acid might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetylsalicylic acid. Contact lenses should not be worn if the potential exists for acetylsalicylic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACROLEIN

INTRODUCTION

This guideline summarizes pertinent information about acrolein for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_4O

- **Structure**

$CH_2{=}CHCHO$

- **Synonyms**

Acraldehyde, acrylic aldehyde, acrylaldehyde, trans-acrolein, allyl aldehyde, propenal, 2-propenal, propylene aldehyde, ethylene aldehyde, Aqualine, Biocide, Crolean, Magnacide

- **Identifiers**

1. CAS No.: 107-02-8
2. RTECS No.: AS1050000
3. DOT UN: 1092 30 (inhibited form)
4. DOT labels: Flammable Liquid, Poison (for the inhibited form)

- **Appearance and odor**

Acrolein is a clear, colorless to yellow, flammable liquid with a disagreeable, choking odor. The odor threshold is reported to be between 0.02 and 0.4 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 56.1
2. Boiling point (760 mm Hg): 52.5°C (126.5°F)
3. Specific gravity (water = 1): 0.84 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acrolein): 1.94
5. Melting point: −87.7°C (−125.9°F)
6. Vapor pressure at 20°C (68°F): 210 mm Hg
7. Solubility: Soluble in water, alcohol, ether, and acetone
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame. The vapors of acrolein form explosive mixtures with air.

2. Incompatibilities: Acrolein is very reactive and polymerizes rapidly and violently in the presence of strong acid or basic catalysts, light, heat, and volatile amines. Upon storage, it forms shock-sensitive and heat-sensitive explosive compounds. Fire and explosions may result from contact of acrolein with oxidizers, acids, alkalies, or ammonia.

3. Hazardous decomposition products: Toxic gases and vapors, including peroxides and oxides of carbon, may be released in a fire involving acrolein.

4. Special precautions: An inhibitor, usually hydroquinone, should be added to this highly unstable material to prevent self-polymerization.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to acrolein.

1. Flash point: −26°C (−15°F) (closed cup)
2. Autoignition temperature: 220°C (428°F)
3. Flammable limits in air (% by volume): Lower, 2.8; upper, 31

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use carbon dioxide, dry chemical, or alcohol foam to extinguish fires involving acrolein. Water may be ineffective, but it may be used to keep fire-exposed containers cool or to protect persons attempting to stop a leak involving this substance.

Fires involving acrolein should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of acrolein may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrolein. Chemical protective clothing specifically recommended for acrolein may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acrolein.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrolein is 0.1 ppm (0.25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 0.3 ppm (0.8 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.25 mg/m^3) as an 8-hr TWA and 0.3 ppm (0.8 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acrolein a threshold limit value (TLV) of 0.1 ppm (0.23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (0.69 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of severe eye, nose, and respiratory irritation associated with exposure to acrolein.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acrolein can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Acrolein is a severe irritant and corrosive to the eyes, skin, mucous membranes, and respiratory tract in animals. Eye contact with liquid acrolein has caused severe burns, corrosion, and corneal injury [Grant 1986; Proctor et al. 1988]. The dermal LD_{50} in rabbits is 562 mg/kg [NIOSH 1991]. Skin contact can cause erythema, edema, severe irritation, corrosion, and burns [NIOSH 1991]. The mouse RD_{50} (concentration that decreases respiratory rate by 50% in exposed animals) is 1.7 ppm [NLM 1992]. The 10-min, 30-min, and 8-hr LC_{50}s in rats are 375, 131, and 8 ppm, respectively [AIHA 1989]. Cats exposed for 3.5 hr to 10 ppm showed signs of respiratory irritation, mild narcosis, lacrimation, and salivation [ACGIH 1991a]. The oral LD_{50} is 42 to 46 mg/kg in rats and 28 mg/kg in mice [AIHA 1989]. When swallowed, acrolein induces gastrointestinal distress, pulmonary congestion, and edema [NLM 1992]. Rats, guinea pigs, dogs, and monkeys were repeatedly exposed to 0.7 or 3.7 ppm for 8 hr/day, 5 days/week for 6 weeks. All animals exposed to 0.7 ppm developed inflammatory lung changes. Emphysema was infrequently but more predominantly observed in dogs and monkeys than in rats or guinea pigs. Animals exposed to 3.7 ppm salivated and had ocular and respiratory irritation. Histopathology of survivors revealed nonspecific inflammatory changes in the lungs, liver, and kidneys. Squamous metaplasia of dog and monkey trachea and necrotizing bronchitis with squamous metaplasia of monkey lungs was also observed. In addition, these four species were continuously exposed to 0.21, 0.23, 1.0, or 1.8 ppm acrolein 24 hr/day for 90 days. Findings similar to those cited for the repeated exposure experiment were likewise observed, with the inflammatory changes also being noted in the brains of all acrolein-exposed animals [Lyon et al. 1970]. Male rats died (32 of 57) following exposures to 4 ppm for 6 hr/day, 5 days/week for 62 exposure days. Terminal histopathology revealed bronchiolar necrosis and pulmonary edema in treated animals [Proctor et al. 1988]. Intra-amniotic or intravenous administration of acrolein to pregnant rats induced malformations or embryolethality, respectively [NIOSH 1991]. Acrolein is mutagenic in bacterial test systems [NIOSH 1991]. Mice that were dermally injected with acrolein for 24 weeks did not develop injection-site sarcomas during the ensuing 70-week observation period [NLM 1992]. Syrian golden hamsters inhaled 4 ppm for 7 hr/day, 5 days/week for 52 weeks. Additional groups were also administered benzo(a)pyrene or

N-nitrosodiethylamine. Following 29 weeks without exposure, terminal sacrifice in week 81 demonstrated that no increased tumor incidence had been induced by acrolein [NLM 1992].

2. *Effects on Humans*: Acrolein is a powerful lacrimating agent and severe tissue irritant. Eye contact with liquid acrolein can cause pain, intense lacrimation, blepharocojunctivitis, swelling of the lids, purulent discharge, photophobia, and corneal injury [Grant 1986; Gosselin et al. 1984; NLM 1992]. Contact of the skin with liquid acrolein causes redness, edema, swelling, vesiculation, and burns. In addition, acrolein can be absorbed through the skin in sufficient amounts to cause systemic effects [Gosselin et al. 1984]. This chemical is a weak skin sensitizer in some exposed individuals [Proctor et al. 1988]. Exposure to 0.25 ppm for 5 min causes moderate irritation of the eyes, mucous membranes, and upper respiratory tract [Clayton and Clayton 1981; Grant 1986]. Exposure to a 1-ppm (2.3-mg/m^3) concentration of acrolein vapor for the same interval is described as intolerable and causes intense lacrimation and severe eye, nose, and throat irritation [Clayton and Clayton 1981; Grant 1986]. Acrolein is a severe lung irritant and tear-inducer at 3 ppm (7 mg/m^3) [IARC 1985]. At higher exposure levels, it can induce significant delayed-onset lung injury, including dyspnea, asthma, congestion, edema, and persistent respiratory insufficiency with decreased pulmonary function [NLM 1992]. Prolonged exposure to 21 ppm causes pulmonary edema, and fatalities have been reported at concentrations as low as 10 ppm; exposure to 150 ppm for 10 min is lethal to humans [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acrolein can cause severe irritation or corrosion of the eyes, nose, throat, and lungs, with tearing, pain in the chest, and delayed-onset pulmonary injury with depressed pulmonary function. Contact of liquid acrolein with the eyes may cause corneal burns, corrosion, and blindness; skin contact may result in redness, swelling, chemical burns with blisters, and corrosion.

2. *Chronic exposure*: The signs and symptoms of chronic exposure to acrolein include skin sensitization and contact dermatitis.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of acrolein! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acrolein are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acrolein or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acrolein and may result in worker exposures to this substance:

- —Use of acrolein as an intermediate in the production of glycerine and methionine analogs (poultry feed protein supplements)
- —Manufacture of colloidal forms of metals, artificial resins, synthetic fibers, and polyurethane foams
- —Chemical synthesis of 1,3,6-hexanetriol, glutaraldehydes, and acrylates
- —Use of acrolein as a slimicide in the manufacture of paper
- —Use of acrolein in biomedical applications to fix tissue and, with its polymers, to immobilize enzymes
- —Subsurface injection of wastewaters to control the growth of microbes in feed lines and to control the growth of algae, aquatic weeds, and mollusks in recirculating process water systems
- —Manufacture of pharmaceuticals, perfumes, and food supplements
- —Use of acrolein as an alcohol denaturant
- —Heating of oils and fats containing glycerol
- —Use of acrolein as a liquid fuel

The following methods are effective in controlling worker exposures to acrolein, depending on the feasibility of implementation:

- —Process enclosure
- —Local exhaust ventilation
- —General dilution ventilation
- —Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrolein, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrolein at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrolein exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acrolein on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrolein.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrolein is determined by using a solid sorbent sampling tube containing 2-(hydroxymethyl)piperidine on XAD-2 adsorbent. Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 48 liters is collected. The sample is then treated with toluene to extract the acrolein. Analysis is conducted by gas chromatography using a nitrogen-phosphorus detector. This method has a sampling and analytical error of 0.12 and is sufficiently sensitive for full-shift personal monitoring below the PEL of 0.1 ppm. For STEL measurements, the limit of the method is 0.8 ppm for a 15-min sample. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 52 of the *OSHA Analytical Methods Manual* [OSHA 1985]. A similar method (Method 2501) can be found in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acrolein contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with acrolein should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrolein, particularly its potential to cause severe irritation of the eyes and skin.

A worker who handles acrolein should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrolein or a solution containing acrolein is handled, processed, or stored.

STORAGE

Acrolein should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Acrolein must be stored under a nitrogen blanket. Uninhibited acrolein may not be stored, and the level of the inhibitor must be checked regularly during prolonged storage. The storage area should be equipped with an automatic sprinkler or other extinguishing system. All electrical service in the storage area must be of explosionproof design. Containers of acrolein should be protected from physical damage and should be stored separately from alkaline materials (such as caustics, ammonia, or amines), oxidizers, heat, sparks, and open flame. To prevent static sparks, containers and equipment should be grounded and bonded when transferring liquid acrolein. Because empty containers formerly containing acrolein may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acrolein, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Provide maximum explosionproof ventilation.

5. If feasible, remove leaking containers to a safe place.

6. Absorb small liquid spills with sand, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the acrolein for later reclamation or disposal, or absorb with vermiculite or sand.

8. After cleanup, the spill area should be washed thoroughly with soap and water.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

If 500 lb or more of acrolein is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acrolein is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acrolein per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrolein emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acrolein is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P003. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acrolein also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrolein exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with acrolein. Impervious clothing, gloves, boots, and other protective clothing are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The only material that has been tested against permeation by acrolein and has demonstrated good-to-excellent resistance for longer than 8 hr is butyl rubber. Natural rubber, neoprene, nitrile, polyvinyl alcohol, polyvinyl chloride, Teflon®, and Viton® have demonstrated poor resistance to permeation by acrolein.

If acrolein is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrolein might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrolein. Contact lenses should not be worn if the potential exists for acrolein exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLAMIDE

INTRODUCTION

This guideline summarizes pertinent information about acrylamide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_5NO

- **Structure**

$H_2C=CHCONH_2$

- **Synonyms**

Acrylic amide; propenamide; 2-propenamide; propenoic acid amide; acrylamide monomer

- **Identifiers**

1. CAS No.: 79-06-1
2. RTECS No.: AS3325000
3. DOT UN: 2074 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Acrylamide is a colorless to white, odorless, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 71.1
2. Boiling point (at 760 mm Hg): 175° to 300°C (347° to 572°F); decomposes on boiling
3. Specific gravity (water = 1): 1.1 at 30°C (86°F)
4. Vapor density (air = 1 at boiling point of acrylamide): 2.4
5. Melting point: 84.5°C (179.3°F)
6. Vapor pressure at 20°C (68°F): 0.007 mm Hg
7. Solubility: Miscible with water; soluble in acetone, ethanol, ethyl ether, and methanol
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Acrylamide decomposes above 175°C (347°F). Violent polymerization may occur when heated or when exposed to ultraviolet light.
2. Incompatibilities: Fires and explosions may result from contact of acrylamide with strong oxidizers.
3. Thermal decomposition products: Toxic gases (such as ammonia, hydrogen, and carbon monoxide) may be released when acrylamide decomposes; toxic oxides of nitrogen may form in fire.
4. Special precautions: None

- **Flammability**

Acrylamide is combustible, but because of its high flash point, it is considered only a slight fire hazard when exposed to heat, sparks, or open flame. It is a combustible, flammable liquid when dissolved in solvent. The National Fire Protection Association has not assigned a flammability rating to

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

acrylamide; other sources rate acrylamide as a moderate fire hazard.

1. Flash point: 138°C (280°F) (closed cup)
2. Autoignition temperature: 424°C (795°F)
3. Flammable limits in air (% by volume): Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam for small fires; water spray, fog, or standard foam for large fires.

Fires involving acrylamide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of acrylamide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool the containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrylamide. Chemical protective clothing specifically recommended for acrylamide may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acrylamide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylamide is 0.03 mg/m^3 as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" designation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.03 mg/m^3 as an 8-hr TWA with a "Skin" notation. However, acrylamide has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated acrylamide an A2 substance (suspected human carcinogen) and assigned acrylamide a threshold limit value (TLV) of 0.03 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of systemic poisoning associated with exposure to acrylamide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acrylamide can occur through inhalation of vapor, dust, or aerosol and absorption through the skin or mucous membranes.

- **Summary of toxicology**

1. *Effects on Animals*: Acrylamide is an irritant, a potent neurotoxin that affects both the central and peripheral nervous systems, a reproductive toxin, and a carcinogen. A 10% aqueous solution of acrylamide applied to abraded rabbit skin caused tissue swelling and redness. Although the 10% aqueous solution immediately caused slight pain and conjunctival irritation, a 40% solution produced severe pain with minimal corneal damage. This damage was repaired within 24 hr following a nonrinsed ocular application [Grant 1986]. Acrylamide is also a moderate skin irritant. The acute dermal LD_{50} in rabbits is 2,250 mg/kg [ACGIH 1991a]. The acute oral LD_{50} for rats, guinea pigs, and rabbits fed aqueous solutions of 2.5% to 12.6% acrylamide ranged from 150 to 180 mg/kg body weight. However, in rats fed a 50% aqueous solution of acrylamide, the LD_{50} was 565 mg/kg and 490 mg/kg for males and females, respectively. The acute lethality of acrylamide is a result of its neurotoxic effects, especially on the central nervous system. The toxic effects of acrylamide on the central nervous system are reversible if the dose and duration of exposure are minimal. Recovery is greatly prolonged if the exposure duration is increased [ACGIH 1991a].

Severe or lethal exposure concentrations can also induce testicular degeneration of the seminephrous tubules, degeneration of the convoluted tubular epithelium of the kidney, fatty degeneration and necrosis of the liver, and congestion of the lungs [NLM 1991]. The primary effects of repeated exposures are neurotoxic and involve the central and peripheral nervous systems. The central nervous system effects predominate during acute and subchronic exposures and can also involve somnolence and hallucinations. The sensory and motor neuronal effects on the peripheral nervous system (such as distal numbness, paresthesias, sensory loss, weakness, ataxia, and paralysis) predominate during chronic exposures [NLM 1991]. Rats, cats, and monkeys have developed neuropathies only when exposed to repeated daily doses of 1 mg/kg or more [ACGIH 1991a].

Male rats and mice that received neurotoxic concentrations of acrylamide orally for 2 to 3 months developed testicular degeneration. The rats consumed 20 mg/kg of body weight per day from drinking water, which contained 400 ppm. The mice received doses of 35.5 mg/kg twice per week [NLM 1991]. Chromosomal alterations in the sperm (but not bone marrow) cells of male DDY mice exposed to acrylamide have also been reported [Sakamoto and Hashimoto 1986]. Although pregnant rats that consumed a diet containing 400 ppm throughout their gestation period developed maternal toxicity (neurotoxicity), only slightly depressed birth weights were noted in their pups [ACGIH 1991a]. Similar consumption of a 200-ppm diet induced an abnormal gait in the pregnant dams but did not affect the growth and development of offspring during their first 6 weeks of postnatal development [ACGIH 1991a]. No developmental defects were induced in fetuses of pregnant dams intubated with 20 mg/kg per day (200 mg/kg total dose) during days 6 to 17 of gestation [NLM 1991].

Studies in mice and rats confirm that acrylamide can act either as an initiator or as a complete carcinogen [NIOSH 1991]. This chemical induces skin-tumor-initiating activity in Sencar mice and lung tumors in A/J mice. Acrylamide administered in drinking water to F344 rats for 2 years caused a statistically increased number of tumors (including cancerous tumors) at multiple sites. The International Agency for Research on Cancer (IARC) found "sufficient evidence of carcinogenicity" for chronically exposed animals [IARC 1986].

2. *Effects on Humans*: Most cases of acrylamide toxicity in humans have resulted from occupational exposures, especially transcutaneous ones. In these cases, episodic contact dermatitis of the hands is usually observed before signs of severe neuropathy become apparent. Workers exposed through the skin to acrylamide dust for 1 to 24 months developed characteristic neurological signs that consisted of postural difficulty, ataxia, lethargy, loss of vibratory sensation, loss of deep tendon reflexes, loss of position sense, and weakness, numbness, and tingling of the extremities. In addition, the extremities were cold and bluish-red in color. The palms of the hands and soles of the feet sweated excessively, and skin peeled from the hands and fingers [Sax 1984; Schaumburg et al. 1983].

Acrylamide toxicity resulting from ingestion of subacute doses (such as in contaminated drinking water) is manifested by central nervous system neuropathy. Drowsiness, disturbed balance, confusion, memory loss, and hallucinations have all been reported following ingestion of acrylamide. Nystagmus and slurred speech have also been noted. Disturbances of vision have not been observed in cases of systemic acrylamide toxicity. In systemic acrylamide poisoning, peripheral neuropathy is late to appear relative to central nervous system effects. The signs and symptoms of acrylamide toxicity remit slowly, and often only partially, following cessation of exposure. Although IARC could find no adequate data that demonstrate an increased cancer incidence in acrylamide-exposed workers, they classify the chemical as 2B, "possibly carcinogenic to humans." This classification is based on the induction of cancers in exposed experimental animals [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Exposure to acrylamide can cause irritation, muscular stiffness and weakness, ataxia, loss of balance, loss of proprioception, and ability to stand.

2. *Chronic exposure*: Exposure to acrylamide can cause irritation, peeling of the skin and excessive sweating of the hands and feet, somnolence, confusion, hallucinations, memory loss, numbness, sensory loss, loss of tendon reflexes, weakness, nystagmus, slurred speech, incoordination, tremor, muscular atrophy, ataxia, and paralysis.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Acrylamide can cause skin irritation. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If respirable acrylamide is inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to swab particulates from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acrylamide is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acrylamide may result in worker exposures to this substance:

—Use in the manufacture of copolymers and polyacrylamides for use as flocculating and thickening agents in pulp and paper industries, oil production, mining textiles, surface coating, adhesives, dyes, photography, and water and waste treatment

—Use as a grouting material in oil wells, basements, tunnels, mine shafts, caissons, and dams

—Use in miscellaneous processes of monomer acrylamide as a curing agent and in organic synthesis

—Use in soap and cosmetic preparations as thickeners and in preshave lotions, hair grooming preparations, and denture fixtures

—Use in stabilizing soil and in permitting the free flow of foundry sand into molds

—Use in clarifying solutions in chemical and food manufacturing; use in gel form in electrophoresis procedures in laboratories

The following methods are effective in controlling worker exposures to acrylamide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrylamide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrylamide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history or findings consistent with seizure or other central nervous system disorders or chronic respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrylamide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acrylamide on the central nervous system and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrylamide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrylamide is determined by using a personal sampling train consisting of a glass fiber filter in a Swinnex cassette (13 mm) followed by a silica gel tube. Plastic cassettes (37 mm) yielded poor recoveries of acrylamide and are therefore unsuitable. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. The silica gel tube should then be treated with methanol to extract the acrylamide. An important step in this method is the transfer of the glass-fiber filters to glass vials containing 1 ml of methanol immediately after sampling to avoid losses of acrylamide from the filter by evaporation. The sample is then analyzed by gas chromatography using a nitrogen/phosphorous detector. The limit of detection for this procedure is 1.3 parts per billion (ppb) (0.004 mg/m^3). This method (Method 21) is included in the OSHA Computerized Information System [OSHA 1986]. The NIOSH procedure (Method S158) is described in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Because acrylamide can be absorbed through the skin in lethal amounts, workers should immediately remove any contaminated clothing and then should wash thoroughly with soap and water any areas of the skin that have come in contact with this substance.

Clothing and shoes contaminated with acrylamide should be removed immediately and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrylamide, particularly its potential for being absorbed through the skin in lethal amounts.

A worker who handles acrylamide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrylamide is handled, processed, or stored.

STORAGE

Acrylamide should be stored in a dark, dry, well-ventilated refrigerated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage in an inert atmosphere is recommended. All electrical service in storage areas should be of explosionproof design. Containers of acrylamide should be protected from physical damage and should be stored separately from oxidizing agents, polymerization catalysts, heat, sparks, and open flame. Because empty containers may contain acrylamide residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acrylamide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Provide maximum explosionproof ventilation.

5. Use nonsparking tools during cleanup.

6. Carefully collect solid material using sand, vermiculite, or soda ash and place in a covered container for disposal.

7. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acrylamide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of acrylamide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrylamide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acrylamide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrylamide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with acrylamide. Gloves, apron, boots, and a chemical protective suit should be worn when workers are handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyethylene/ethylene vinyl alcohol has been tested against permeation by acrylamide and has demonstrated good-to-excellent resistance for periods of 4 to 8 hr.

If acrylamide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrylamide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrylamide. Contact lenses should not be worn if the potential exists for acrylamide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLIC ACID

INTRODUCTION

This guideline summarizes pertinent information about acrylic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_4O_2$

- **Structure**

$CH_2{=}CHCO_2H$

- **Synonyms**

Propenoic acid, acroleic acid, ethylenecarboxylic acid, propene acid, vinylformic acid, glacial acrylic acid, 2-propenoic acid

- **Identifiers**

1. CAS No.: 79-10-7
2. RTECS No.: AS4375000
3. DOT UN: 2218 29
4. DOT label: Corrosive

- **Appearance and odor**

Acrylic acid is a colorless, corrosive, combustible liquid with a distinctive and acrid odor. The odor threshold is reported to be 1.0 part per million (ppm) parts of air. Acrylic acid is available commercially in the United States in two forms: the technical grade (which contains 94% acrylic acid) and glacial acrylic acid (which contains 98% acrylic acid).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72.1
2. Boiling point (760 mm Hg): 141°C (221.8°F)
3. Specific gravity (water = 1): 1.06 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acrylic acid): 2.5
5. Melting point: 14°C (57.2°F)
6. Vapor pressure at 20°C (68°F): 3.1 mm Hg
7. Solubility: Miscible with water, alcohol, ether, acetone, and benzene
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: The vapor forms an explosive mixture in contact with the air. Heat, sparks, open flame, oxygen, high temperature, and pressure.
2. Incompatibilities: Fires and explosion may result from contact of acrylic acid with oxydizing agents, amines, alkalis, ammonium hydroxide, chlorosulfonic acid, ethylene diamine, ethyleneimine, oleum, or 2-aminoethanol.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving acrylic acid.
4. Special precautions: Acrylic acid corrodes carbon steel and other metals.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to acrylic acid.

1. Flash point: 50°C (122°F) (open cup)
2. Autoignition temperature: 438°C (820°F)
3. Flammable limits in air (% by volume): Lower, 2.4; upper, 8.0
4. *Extinguishant:* Use dry chemical, water spray, alcohol foam, or carbon dioxide to fight fires involving acrylic acid.

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Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving acrylic acid should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acrylic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrylic acid. Firefighters' protective clothing may not provide protection against permeation by acrylic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylic acid is 10 ppm (30 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (6 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1988, 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acrylic acid a threshold limit value (TLV) of 2 ppm (5.9 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991]. The ACGIH TLV also bears a "Skin" notation.

- **Rationale for limits**

The OSHA limit was established to protect workers from the risk of eye and nasal irritation. The NIOSH and ACGIH limits were based on recent studies demonstrating degeneration of nasal mucosa at 5 ppm, changes in pulmonary function, teratogenicity and embryotoxicity in rats at low doses, and skin absorption in animals.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acrylic acid can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: Acrylic acid is dermally absorbed and is corrosive to the eyes, nose, and mucous membranes in animals. Application of glacial acrylic acid to the eyes of rabbits caused irreversible corneal injury graded 9 on an ascending severity scale of 1 to 10 [Grant 1986]. Application of a 1% solution to the eye of a rabbit caused severe burns and eye injury [ACGIH 1991a; NIOSH 1991; Proctor et al. 1988]. Irreversible eye and skin damage resulted following exposure of rats to 1,200 ppm for 4 hr [NLM 1992]. Applied to rabbit skin, acrylic acid caused severe irritation [Proctor et al. 1988]. Three of five guinea pigs became dermally sensitized when exposed to acrylic acid by injection and subsequently challenged with this substance [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 290 mg/kg [NLM 1992]. Saturated atmospheres have been reported to range from 420 ppm at 20° to 760 ppm at 30° [NLM 1992]. Although exposure of rats to polymerized saturated vapors (room temperature) for 8 hr did not induce deaths [Smyth et al. 1962], a 1-hr exposure to unpolymerized saturated vapor was the maximum duration tolerated without death [Carpenter et al. 1974]. Vapor concentrations approaching saturation killed half of a group of rats exposed for 3.5 hr [NLM 1992]. However, 4-hr exposures of rats at 2,000 or 4,000 ppm were nonlethal [NLM 1992; Carpenter et al. 1974]. The 4-hr LC_{50} in rats is 1,200 ppm [NLM 1992]. Exposure of rats to irritant concentrations of acrylic acid caused decreased respiratory rates and tidal and minute volumes [ACGIH 1991a]. In addition, four rats exposed once to 6,333 ppm of acrylic acid for 5 hr developed eye and nose irritation, respiratory difficulties, and unresponsivness; one animal died. At autopsy, these animals showed lung, liver, and kidney damage [ACGIH 1991a]. The oral LD_{50} in rats was variable: 357, 1,250, or 2,722 mg/kg [NLM 1992; Smyth et al. 1962]. Rats exposed to acrylic acid at 80 ppm for 6 hr/day, 5 days/week for 4 weeks showed no adverse effects, and rats exposed to 300 ppm on the same regimen experienced nose irritation, lethargy, and decreased weight

gain. Rats exposed to 1,500 ppm acrylic acid for shorter intervals showed damage to the liver, kidneys, and lungs at autopsy [ACGIH 1991a]. However, rats that inhaled 233 ppm for 4 hr/day, 5 days/week for 4 weeks developed gastric mucosal lesions and pulmonary inflammation [NLM 1992]. In rats exposed to the vapors of acrylic acid at 5, 25, or 75 ppm for 6 hr/day, 5 days/week for 13 weeks, terminal pathology was normal in the 5- or 25-ppm group; however, slight degenerative lesions of the olfactory mucosa were present in the high-dose group [ACGIH 1991a]. Similarly exposed mice were more sensitive than rats as they developed lesions of the nasal mucosa for all three exposure concentrations [ACGIH 1991a]. Intraperitoneal or intra-amniotic injections of acrylic acid caused embryotoxicity and gross abnormalities in the offspring of treated pregnant rats [Proctor et al. 1988; NLM 1992].

2. *Effects on Humans*: Acrylic acid is corrosive on contact with the eyes, skin, mucous membranes, and upper respiratory tract of humans, and its vapor causes severe irritation of these organs. Acute industrial exposure to this substance has caused eye and skin burns ranging in intensity from moderate to severe [Proctor et al. 1988]. Absorption of acrylic acid through the skin has been reported to cause systemic illness, and inhalation of the mist or vapor of acrylic acid may cause lung injury as well as nasal irritation and tearing of the eyes [Genium 1989]. Based on effects seen in animals, acrylic acid may cause skin sensitization [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acrylic acid can cause redness, swelling, and tearing of the eyes, runny nose, scratchy throat, coughing, and difficult breathing. Contact of the liquid with the eyes or skin can cause corneal injury, irritation, burns, and destruction of the tissue.

2. *Chronic exposure*: Chronic exposure to acrylic acid may cause lethargy, irritation, and skin sensitization reactions.

- **Emergency procedures**

WARNING!

[illegible]

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. *Immediately* initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of acrylic acid. ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acrylic acid are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acrylic acid or a solution containing it is ingested:

—Seek medical attention ***immediately***.

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acrylic acid and may result in worker exposures to this substance:

—Manufacture of acrylic resins, especially the acrylates

—Use of acrylic acid in acrylic polymeric emulsions for leather, textile, and paper coatings

—Use of acrylic acid in paints, floor polishes, adhesives, general finishes, and binders

—Manufacture of plastics, molding powder for signs, construction units, decorative emblems, and insignia

—Use of acrylic acid in dentistry and medicine

The following methods are effective in controlling worker exposures to acrylic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrylic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrylic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acrylic acid on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrylic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrylic acid is determined by using two XAD-8 tubes connected in series. Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 24 liters is collected. The sample is then treated with methanol and water (1:1) to extract the acrylic acid. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method has a sampling and analytical error of 0.12 and is found in OSHA Method No. 28, *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If acrylic acid contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, followed by washing with soap and water.

Clothing contaminated with acrylic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrylic acid, particularly its potential to cause skin burns.

A worker who handles acrylic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrylic acid or a solution containing acrylic acid is handled, processed, or stored.

STORAGE

Acrylic acid is explosive unless (1) an inhibitor has been added to it before it is stored, or (2) it is stored at temperatures below its melting point. Acrylic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; the storage area must meet the requirements for an OSHA Class II combustible liquid. Explosionproof exhaust ventilation and sparkproof fans must be used in storage areas. Storage tanks should be made of stainless steel or aluminum. Containers of acrylic acid should be protected from physical damage and should be stored separately from oxidizers, amines, alkalies, other incompatible substances, heat, sparks, and open flame. Only nonsparking tools may be used to handle acrylic acid. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained acrylic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acrylic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Use water spray to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. Use nonsparking tools for cleanup.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the acrylic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acrylic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulation resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acrylic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acrylic acid per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrylic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acrylic acid is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U008. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acrylic acid may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrylic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910. 134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any possibility of skin contact with acrylic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acrylic acid and have demonstrated good-to-excellent resistance for periods greater than 8 hr: butyl rubber and Saranex®. Materials that may withstand permeation for more than 4 hr but fewer than 8 hr: Teflon® and Viton®. Natural rubber, neoprene, nitrile rubber, polyethylene, and polyvinyl chloride have demonstrated poor resistance to permeation by acrylic acid.

If acrylic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrylic acid might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrylic acid. Contact lenses should not be worn if the potential exists for acrylic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLONITRILE

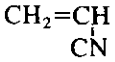
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about acrylonitrile for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_3H_3
- **Structure:**



$CH_2{=}\underset{CN}{CH}$

- **Synonyms:** Acrylon, AN, carbacryl, cyanoethylene, fumigrain, propenenitrile, VCN, ventox, vinyl cyanide
- **Identifiers:** CAS 107-31-1; RTECS AT5250000; DOT 1093, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Pale yellow liquid with an unpleasant odor similar to pyridine

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 53.07
2. Boiling point (at 760 mmHg): 77.3°C (171°F)
3. Specific gravity at 20°C (68°C) (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of acrylonitrile): 1.83
5. Melting point: -83°C (-117°F)
6. Vapor pressure at 20°C (68°F): 83 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 7.35
8. Evaporation rate (butyl acetate = 1): 4.54
9. Saturation concentration in air (approximate) at 20°C (68°F): 10.9% (109,000 ppm)
10. Ionization potential: 10.91 eV

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers, especially bromine, and strong bases may cause fires and explosions. Contact with copper, copper alloys, ammonia, or amines may cause decomposition. Acrylonitrile will polymerize when hot, and the additional heat liberated by the polymerization may generate high internal pressure and cause containers to explode. Inhibitors are added to the commercial product to prevent self-polymerization.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving acrylonitrile.
3. Caution: Acrylonitrile will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -1°C (30°F) (closed cup)
2. Autoignition temperature: 481°C (898°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 17
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: Approximately 20 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylonitrile is 2 parts of acrylonitrile per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the OSHA ceiling concentration which shall at no time be exceeded is 10 ppm as determined in any 15-minute sampling period (Skin). The notation for "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that acrylonitrile be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 1 ppm as a TWA for up to an 8-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 10 ppm as determined in any 15-minute sampling period (Skin). The American Conference of Governmental In-

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dustrial Hygienists (ACGIH) has designated acrylonitrile as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 2 ppm [4.5 milligrams of acrylonitrile per cubic meter of air (4.5 mg/m³)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational Exposure Limits for acrylonitrile

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA (Skin)*	2	—
Ceiling (15 min) (Skin)	10	—
NIOSH REL TWA (Skin) (Ca)†	1	—
Ceiling (15 min) (Skin)	10	—
ACGIH TLV® TWA (Skin) (A2)§	2	4.5

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Acrylonitrile may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats, guinea pigs, or dogs, acute inhalation or oral administration of acrylonitrile caused signs of toxicity including decreased water and food consumption, decreased weight gain, histologic changes in the brain resembling anoxia, or damage to the lungs, liver, or kidneys. In rats, chronic inhalation or oral administration of acrylonitrile produced tumors of the brain, stomach, ear canal, and mammary glands, and cancer of the Zymbal gland. Oral administration of acrylonitrile to pregnant rats caused embryotoxic and teratogenic effects.
2. *Effects on humans:* Two separate studies of workers who were potentially exposed to acrylonitrile and who were observed over an 18- or 20-year period showed increased incidences of lung and colon cancers. In addition, at least two deaths from accidental inhalation or skin absorption of acrylonitrile have occurred.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to acrylonitrile can cause eye irritation, headache, sneezing, nausea, vomiting, weakness, light-headedness, and asphyxia.
2. *Long-term (chronic):* Skin contact with acrylonitrile can cause burns, blisters, and dermatitis.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to acrylonitrile, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to acrylonitrile at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis, and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to acrylonitrile. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination.
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to acrylonitrile may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events
Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation
Measurements to determine worker exposure to acrylonitrile should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• Ceiling concentration evaluation
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of acrylonitrile. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• Method
Sampling and analysis may be performed by collecting acrylonitrile vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure acrylonitrile may also be used if available. A detailed sampling and analytical method for acrylonitrile may be found in the *NIOSH Manual of Analytical Methods* (method number 1604).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with acrylonitrile.

SANITATION

Clothing which is contaminated with acrylonitrile should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of acrylonitrile from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of acrylonitrile's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with acrylonitrile should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle acrylonitrile should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to acrylonitrile may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for acrylonitrile

Operations	Controls
During use in the manufacture of ABS resin, SAN resin, plastic, or surface coating materials	Total enclosure
During the manufacture and transfer of monomer to other reaction vessels or to tank cars.	Total enclosure, local exhaust ventilation, personal protective equipment
During use as a chemical intermediate; during use in the cyanoethylation of cotton	Local exhaust ventilation, personal protective equipment
During use in surface coating applications	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to acrylonitrile, an eye-wash fountain should be provided within the immediate work area for emergency use.

If acrylonitrile gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to acrylonitrile, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If acrylonitrile gets on the skin, wash it immediately with soap and water. If acrylonitrile penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If acrylonitrile is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing acrylonitrile, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing acrylonitrile may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing acrylonitrile may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for acrylonitrile

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR

ALDRIN

POTENTIAL HUMAN CARCINOGEN

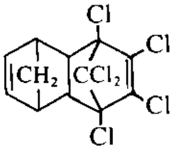
INTRODUCTION

This guideline summarizes pertinent information about aldrin for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

NOTE: Most uses of aldrin were suspended by the U.S. Environmental Protection Agency, effective October 18, 1974. The only uses allowed are direct soil application, seed treatment if labeled "not for food use," dipping of plant roots and tops, subsurface termite control, and hot-caps.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_8Cl_6$
- **Structure:**



- **Synonyms:** Aldrex; aldrine; aldrosol; octalene; 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene
- **Identifiers:** CAS 309-00-2; RTECS IO2100000; DOT 2761, label required: "Poison"
- **Appearance and odor:** Light to dark brown crystals with a mild chemical odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 364.90
2. Boiling point (at 760 mmHg): Decomposes
3. Specific gravity (water = 1): 1.6
4. Melting point: 104°C (219°F)
5. Vapor pressure at 20°C (68°F): 6.0×10^{-6} mmHg
6. Solubility in water: 0.027 mg/l at 27°C (80.6°F)

- **Reactivity**

1. Incompatibilities: Aldrin may react with concentrated mineral acids, acid catalysts, acid oxidizing agents, phenols, or reactive metals.
2. Hazardous decomposition products: Hydrochloric acid fumes and other chlorinated decomposition products may be released in a fire involving aldrin.
3. Caution: Aldrin should be stored in tightly closed containers in a well-ventilated area.

- **Flammability**

Aldrin is nonflammable.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for aldrin is 0.25 milligrams of aldrin per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that aldrin be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.15 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.25 mg/m^3 (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for aldrin

	Exposure limits mg/m^3
OSHA PEL TWA (Skin)*	0.25
NIOSH REL TWA (Ca)†	§0.15
ACGIH TLV® TWA (Skin)	0.25

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ Lowest reliably detectable level.

HEALTH HAZARD INFORMATION

• Routes of exposure

Aldrin may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact. Dermal absorption is substantially increased when aldrin is dissolved in organic solvents.

• Summary of toxicology

1. *Effects on animals:* Acute or chronic oral administration of aldrin to dogs and rats produced liver and kidney degeneration; chronic oral administration produced liver cancer in mice and thyroid cancer in rats. Aldrin fed to pregnant hamsters and mice caused increased fetal deaths, as well as congenital anomalies and growth retardation in the offspring.
2. *Effects on humans:* Aldrin is a neurotoxin and has caused electroencephalogram abnormalities following short-term or long-term oral, dermal, or inhalation exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to aldrin can cause hyperirritability, headache, dizziness, nausea, vomiting, blood in the urine, tremors, convulsions, and coma.
2. *Long-term (chronic):* Exposure to aldrin can cause redness of the skin and dermatitis, weight loss, muscular twitching, and convulsions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to aldrin, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, endocrine glands, and hematopoietic (blood-cell-forming), reproductive, and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to aldrin at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include: preexisting chronic diseases of the skin, liver, kidneys, endocrine glands, and hematopoietic, reproductive, and nervous systems. Workers should inform their physicians of their potential for exposures to aldrin because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter." The physician should obtain baseline values for liver function tests and a complete blood count with reticulocyte count.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to aldrin. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, eyes, liver, kidney, and hematopoietic, reproductive, and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to aldrin may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Non-autoimmune hemolytic anemia.
2. Delayed-onset SHE's include: Cataract, toxic hepatitis, and non-autoimmune hemolytic anemia.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to aldrin should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting aldrin with a glass-fiber filter and a midget impinger containing isooctane. The filter is extracted using isooctane, and analysis is performed using a gas chromatograph with an electrolytic conductivity detector. A detailed sampling and analytical method for aldrin may be found in the *NIOSH Manual of Analytical Methods* (method number 5502).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with aldrin.

SANITATION

Clothing which is contaminated with aldrin should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of aldrin from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of aldrin's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with aldrin should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle aldrin should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to aldrin may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for aldrin

Operations	Controls
During formulation and handling of insecticide	Personal protective equipment, local exhaust ventilation
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to aldrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

If aldrin gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to aldrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If aldrin gets on the skin, wash it immediately with soap and water. If aldrin penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If aldrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Aldrin solid may be collected and placed in an appropriate container.
3. Aldrin solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system.
4. For small quantities of liquids containing aldrin, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing aldrin may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for aldrin

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about allyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_6O

- **Structure**

$CH_2{=}CHCH_2OH$

- **Synonyms**

3-Hydroxypropene, 1-propene-3-ol, propenol, 2-propenol, 2-propenyl alcohol, allylic alcohol, 2-propene-1-ol, vinyl carbinol, Weed Drench

- **Identifiers**

1. CAS No.: 107-18-6
2. RTECS No.: BA5075000
3. DOT UN: 1098 57
4. DOT labels: Flammable Liquid, Poison

- **Appearance and odor**

Allyl alcohol is a clear, colorless, flammable liquid with a pungent, mustardlike odor. The odor threshold is reported to be below 0.8 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58.1
2. Boiling point (at 760 mm Hg): 96°C (205°F)
3. Specific gravity (water = 1): 0.85 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of allyl alcohol): 2.0
5. Melting point: −129°C (−200.2°F)
6. Vapor pressure at 20°C (68°F): 19 mm Hg
7. Solubility: Miscible with water, alcohol, chloroform, ether, and petroleum ether
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame
2. Incompatibilities: Fire and explosion may result from contact of allyl alcohol with carbon tetrachloride, chlorosulfonic acid, diallyl phosphite plus phosphorus trichloride, nitric acid, oleum, sodium hydroxide, sulfuric acid, tri-n-bromomelamine, metal halides, caustic soda, or sodium, potassium, magnesium, aluminum, or their alloys.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be produced when allyl alcohol decomposes.
4. Special precautions: Allyl alcohol attacks some coatings and forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to allyl alcohol.

1. Flash point: 21.1°C (70°F) (closed cup)
2. Autoignition temperature: 378.3°C (713°F)

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air (% by volume): Lower, 2.5; upper, 18.0

4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving allyl alcohol. Water may be ineffective, but it may be used to keep fire-exposed containers cool. If a leak or a spill has not ignited, water spray should be used to disperse the vapors and protect the individuals attempting to stop the leak.

Fires involving allyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of allyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving allyl alcohol. Chemical protective clothing that is specifically recommended for allyl alcohol may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by allyl alcohol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for allyl alcohol is 2 ppm (5 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 4 ppm (10 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (5 mg/m^3) as an 8-hr TWA and 4 ppm (10 mg/m^3) as a STEL with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned allyl alcohol a threshold limit value (TLV) of 2 ppm (4.8 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation and a STEL of 4 ppm (9.5 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of systemic effects and irritation associated with exposure to allyl alcohol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to allyl alcohol can occur through inhalation, ingestion, or contact with the skin, eyes, or mucous membranes. Allyl alcohol is rapidly absorbed through the skin.

• Summary of toxicology

1. *Effects on Animals*: Allyl alcohol is a severe irritant of the eyes, nose, upper respiratory tract, and skin in animals; it also causes neurotoxic effects by all routes of exposure [Clayton and Clayton 1981]. Contact of this substance with the eyes of rabbits caused transitory corneal opacity, and skin contact caused mild irritation [NIOSH 1991; Grant 1986]. Although the 4- and 8-hr LC_{50}s in rats are 165 and 76 ppm, respectively, the lowest 4-hr lethal concentration in monkeys is 1,000 ppm [NIOSH 1991]. Rats acutely exposed to 3.9 ppm (a concentration capable of depressing the respiration rate by 50%) exhibited no signs of pulmonary irritation at necropsy [NLM 1991]. Animals sacrificed following acute inhalation showed signs of pulmonary edema and liver congestion and damage at autopsy [Proctor et al. 1988]. When rats were administered allyl alcohol and allowed 96 hr to recover before sacrifice, they developed acidophilia, vacuolation, and necrosis of the pancreatic acinar cells [NLM 1991]. The lowest reported oral LD_{50} in rats is 64 mg/kg [NIOSH 1991]. The dermal LD_{50} in rabbits is 45 mg/kg [NIOSH 1991]. Rats, rabbits, guinea pigs, and dogs exposed to 7 ppm for 7 hr/day during a 6-month period developed cloudy swelling and focal necrosis of the liver plus necrosis of the renal convoluted tubules. These effects were mild and reversible when exposure was discontinued [NLM 1991]. Rats that consumed drinking water containing allyl alcohol (100, 200, or 800 ppm for 15 weeks) had a dose-related decrease in water intake, food consumption, and weight gain but an increase in terminal organ weights for the liver, spleen, and kidneys [NLM 1991]. Allyl alcohol is directly mutagenic in some bacterial test systems [NIOSH 1991; NLM 1991].

2. *Effects on Humans*: Allyl alcohol is a severe irritant of the eyes, nose, upper respiratory tract, and skin in humans;

this substance can be absorbed through the skin in sufficient amounts to cause systemic toxicity. One man was temporarily blinded after being exposed to the vapor of allyl alcohol [Clayton and Clayton 1981]. Irritation of the eyes with tearing is noticeable at 5 ppm in some individuals, and irritation of the nose and throat begins at 10 to 15 ppm [ACGIH 1991a; Grant 1986]. Allyl alcohol is well absorbed through the skin, producing deep muscle pain believed to be caused by muscle spasm [Clayton and Clayton 1981]. In contact with the skin, allyl alcohol causes chemical burns with vesiculation and superficial necrosis [NLM 1991]. Inhalation exposures may lead to pulmonary edema [NLM 1991]. One worker died following a 1-hr exposure to 1,000 ppm [NIOSH 1991]. Systemic toxicity is manifested in humans as visceral congestion, periportal congestion of the liver, nephritis, and blood in the urine [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to allyl alcohol can cause irritation of the nose, throat, and lungs, and severe overexposure may lead to pulmonary edema with slowly developing distress. Burns and corrosion of the skin plus muscle pain can occur following prolonged contact with the liquid. Exposure of the eyes to liquid or vapor causes irritation, tearing, pain behind the eyeballs, transient corneal injury, and blurred vision and photophobia during exposure to light.

2. *Chronic exposure*: No signs or symptoms of chronic allyl alcohol exposure have been reported, but it may exacerbate chronic respiratory, liver, and kidney disease.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of allyl alcohol. ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of allyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if allyl alcohol or a solution containing it is ingested:

—Seek medical attention ***immediately***.

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve allyl alcohol and may result in worker exposures to this substance:

—Preparation of various allyl esters that serve as monomers and prepolymers in the manufacture of resins and plasticizers

—Use of allyl alcohol as a chemical intermediate

—Manufacture of pharmaceuticals and military poison gas

—Use of allyl alcohol as a fungicide, herbicide, and nematicide

—Manufacture of flavorings, perfumes, allyl esters, glycerol, acrolein, and glycerin

The following methods are effective in controlling worker exposures to allyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to allyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory tract, kidney, and liver. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to allyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, respiratory, kidney, or liver disease.

• Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to allyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of allyl alcohol on the eyes, skin, respiratory system, kidneys, and liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although alcohols can be detected in the blood and urine of exposed individuals, no biological monitoring test acceptable for routine use has yet been developed for allyl alcohol.

• Medical examinations recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne allyl alcohol is determined by using a solid sorbent tube (100/50-mg sections, 20/40 mesh) filled with coconut shell charcoal. Samples are collected at a maximum flow rate of 0.2 liter/min until a minimum air volume of 10 liters is collected. The sample is then treated with a carbon disulfide/dimethylformamide solution to extract the allyl alcohol. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.18. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 1402 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Because allyl alcohol can be absorbed through the skin in lethal amounts, workers should immediately and thoroughly wash with soap and water any areas of the skin that have come in contact with this substance.

Clothing and shoes contaminated with allyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of allyl alcohol, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles allyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where allyl alcohol or a solution containing allyl alcohol is handled, processed, or stored.

STORAGE

Allyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room that is separated from all oxidizing agents. Storage facilities and electrical service should be appropriate for this OSHA Class IB flammable liquid [29 CFR 1910.106]. Containers of allyl alcohol should be protected from physical damage and should be stored separately from oxidizing agents, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded when this substance is transferred from one container to another. Only nonsparking tools may be used to handle allyl alcohol. Because empty containers that formerly contained allyl alcohol may contain product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving allyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors if the spill or leak has not ignited.
6. Absorb small spills with vermiculite, sand, or other noncombustible materials and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the allyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

If 1,000 lb or more of allyl alcohol is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulation resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for allyl alcohol is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of allyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Allyl alcohol is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P005. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Allyl alcohol may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of allyl alcohol are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous substances to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of allyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Because allyl alcohol can be absorbed through the skin in lethal amounts, protective clothing should be worn to prevent skin contact. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by allyl alcohol and have demonstrated good-to-excellent resistance: butyl rubber, Viton®, and Teflon®. Both butyl rubber and Teflon may provide more than 8 hr of resistance to permeation by allyl alcohol. Neoprene, natural rubber, and polyvinyl alcohol have demonstrated poor resistance to permeation by allyl alcohol.

Safety glasses, goggles, or face shields should be worn during operations in which allyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with allyl alcohol. Contact lenses should not be worn if the potential exists for allyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about allyl chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_5Cl

- **Structure**

$CH_2{=}CHCH_2Cl$

- **Synonyms**

3-Chloropropene, 1-chloro-2-propene, α-chloropropylene, chlorallylene, 3-chloropene, 3-chloro-1-propene, 3-chloropropylene, 2-propenyl chloride

- **Identifiers**

1. CAS No.: 107-05-1
2. RTECS No.: UC7350000
3. DOT UN: 1100 57
4. DOT labels: Flammable Liquid, Poison

- **Appearance and odor**

Allyl chloride is a colorless, yellow, or purple liquid with an unpleasant, garliclike odor. The odor threshold is reported to be 0.47 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76.5
2. Boiling point (at 760 mm Hg): 44° to 45°C (111.2° to 113°F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of allyl chloride): 2.6
5. Melting point: −134.5°C (−209°F)
6. Vapor pressure at 20°C (68°F): 295 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, chloroform, ether, and petroleum ether
8. Evaporation rate (butyl acetate = 1): Approximately 7

- **Reactivity**

1. Conditions contributing to instability: Violent polymerization and explosions may occur when allyl chloride is heated or comes into contact with acid catalysts, ferric chloride, aluminum chloride, Lewis acids, or Ziegler-type initiators.
2. Incompatibilities: Fires and explosions may result from contact of allyl chloride with ethylene diamine, ethyleneimine, oleum, chlorosulfonic acid, or with benzene or toluene in the presence of ethyl aluminum dichloride or ethyl aluminum sesquichloride.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving allyl chloride.
4. Special precautions: Allyl chloride attacks some coatings and some forms of plastic and rubber. This substance is also highly corrosive to steel.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to allyl chloride.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: −31.7°C (−25°F) (closed cup)

2. Autoignition temperature: 391°C (737°F)

3. Flammable limits in air (% by volume): Lower, 3.3; upper, 11.1

4. Extinguishant: Use carbon dioxide, dry chemical, or alcohol foam to extinguish fires involving allyl chloride; do ***not*** use a solid stream of water because the stream will scatter and spread the fire.

Fires involving allyl chloride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of allyl chloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a cylinder becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving allyl chloride. Chemical protective clothing that is specifically recommended for allyl chloride may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by allyl chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for allyl chloride is 1 ppm (3 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 2 ppm (6 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (3 mg/m^3) as a TWA for an 8-hr workshift and a 40-hr workweek and 2 ppm (6 mg/m^3) as a STEL [NIOSH 1988].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned allyl chloride a threshold limit value (TLV) of 1 ppm (3 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 2 ppm (6 mg/m^3) for periods not to exceed 15 min. The TLV also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overexposure [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of liver and kidney damage, and neuropathic effects associated with exposure to allyl chloride. The TLV also recommends a "Skin" notation; however, the TLV Committee has solicited quantitative data to serve as a basis for further evaluating the need for a "Skin" notation [ACGIH 1991a].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to allyl chloride can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Allyl chloride is an irritant of the eyes, mucous membranes, and skin in animals; chronic exposure causes liver, kidney, lung, and nervous system damage. When instilled into the eyes of rabbits, allyl chloride caused damage rated as 2 on an ascending severity scale of 1 to 10 [Grant 1986]. Prolonged contact of allyl chloride with the skin causes moderate irritation [Clayton and Clayton 1981; NIOSH 1991]. The maximum acute allyl chloride exposures survived by rats were 29,300 ppm for 15 min, 2,900 ppm for 1 hr, and 290 ppm for 3 hr [NLM 1992]. Mice and rats have also survived 6-hr acute exposures of 800 ppm but not 1,000 to 2,000 ppm. The no-effect level in rats was 200 ppm, and dose-related kidney damage was induced in mice and rats exposed to ≥500 and 300, respectively [ACGIH 1991a]. One of six rats died following an acute 4-hr exposure of 2,000 ppm [Smyth and Carpenter 1948]. The 2-hr LC_{50} was 3,514 ppm in rats and 3,674 ppm in mice. The target organs of toxicity were the liver, kidneys, nervous system, and lungs [ACGIH 1991a]. Rats exposed to 16,000 ppm for 2 hr developed eye and nose irritation, weakness, incoordination, drowsiness, and dyspnea before death. Histopathology at autopsy revealed pulmonary hemorrhage, severe kidney damage, and mild liver injury [Proctor et al. 1988]. Tissue burns and pulmonary edema may develop on a delayed basis [NLM 1992]. The dermal LD_{50} in rabbits is 2,063 mg/kg [Smyth and Carpenter 1948]. In prolonged contact with the skin, allyl chloride caused moderate irritation [Grant 1986]. The oral LD_{50} in rats is

700 mg/kg [Smyth and Carpenter 1948]. Rats, guinea pigs, rabbits, and dogs exposed to allyl chloride at 8 ppm for 7 hr/day for 1 month were asymptomatic but had liver and kidney necrosis at autopsy [Clayton and Clayton 1981]. When these animals were exposed at 3 ppm on the same regimen for 6 months, no exposure-related effects were seen at autopsy (except for reversible liver effects in female rats) [Clayton and Clayton 1981]. Allyl chloride was neurotoxic in multiple species by inhalation, gavage, and parenteral routes of administration. The neurotoxicity has been classified as a degenerative central-peripheral distal axonopathy [ACGIH 1991a]. Allyl chloride was embryotoxic and had developmental effects in rats and mice exposed by inhalation, or by oral or intraperitoneal routes of administration [NIOSH 1991]. Allyl chloride was fetotoxic in rats exposed to 300 ppm, but not in rats exposed to 30 ppm. The chemical was not fetotoxic in rabbits or embryotoxic or teratogenic in rats or rabbits following inhalation of 30 or 300 ppm for 7 hr/day on gestation days 6 to 15 (rats) or 6 to 18 (rabbits) [NLM 1992]. Allyl chloride is mutagenic in *Salmonella typhimurium* and induces gene conversions in *Saccharomyces cerevisiae* [NLM 1992]. It has also been tested for carcinogenicity in mice by several routes of exposure: gavage, skin application, and intraperitoneal injection. A nonsignificant increase in metastasizing squamous cell carcinomas was noted in the forestomachs of mice treated by gavage with doses ranging from 129 to 258 mg/kg. No skin tumors resulted from repeated skin applications; however, allyl chloride acted as an initiator in mice receiving single dermal applications in two-stage carcinogenesis assays. Mice given intraperitoneal injections of allyl chloride showed a significant increase in the incidence of lung adenomas [IARC 1985]. Rats treated by gavage with doses ranging from 55 to 71 mg/kg showed no increase in the incidence of tumors [IARC 1985]. On the basis of these studies, the International Agency for Research on Cancer (IARC) has concluded that there is insufficient evidence that allyl chloride is a carcinogen in treated animals [IARC 1985].

2. *Effects on Humans*: Allyl chloride is an irritant of the eyes, mucous membranes, upper respiratory tract, and skin in humans. Exposure to 25 ppm causes nasal irritation; 50 to 100 ppm causes eye irritation; and concentrations greater than these result in eye pain, conjunctivitis, sensitivity to light, and corneal burns [Grant 1986; Clayton and Clayton 1981; NLM 1992]. Exposure to saturated vapors for a few minutes can be life-threatening [NLM 1992]. Prolonged skin contact may cause a painful sensation described as a deep "bone ache" [Clayton and Clayton 1981]. Other signs and symptoms of chronic exposure have included headache, dizziness, vertigo, nausea, vomiting, proteinuria, hematuria, electrolyte elevations, increased glomerular filtration rates, severe kidney injury, and polyneuropathies [NLM 1992]. Workers exposed to concentrations of allyl chloride above 3 mg/m^3 (1 ppm) demonstrated evidence of kidney dysfunction; exposures to unspecified concentrations were reported to impart a garlic odor to the breath and skin of exposed workers and to alter the results of their liver function tests [Clayton and Clayton 1981]. Exposed female workers had decreased maximum ventilatory capacities [NLM 1992]. Workers exposed to allyl chloride concentrations ranging from 1 to 113 ppm for 16 months showed clinical signs of reversible liver damage as these signs subsided following cessation of exposure [IARC 1985]. Weakness, paresthesia, numbness, and distal neuropathy have been seen in chronically exposed workers; removal from exposure caused a reversal of their neurotoxic signs and symptoms [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Exposure to allyl chloride can cause irritation of the eyes, with redness, pain, conjunctivitis, corneal burns, and a sensitivity to light that may not be manifested for several hours after exposure; irritation of the upper respiratory tract, with coughing, difficult breathing, and delayed-onset pulmonary edema; and redness and irritation of the skin.

2. *Chronic exposure*: Exposure to allyl chloride can cause irritation of tissues including the respiratory tract mucosa, photophobia, headache, dizziness, vertigo, nausea, vomiting, dyspnea, deep bone or muscle pain caused by prolonged skin contact, and numbness, weakness, and tingling or prickly sensations in the hands and feet.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of allyl chloride. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of allyl chloride are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if allyl chloride or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve allyl chloride and may result in worker exposures to this substance:

—Manufacture of glycerin, epichlorohydrin, allyl alcohol, allyl amines, allyl silanes, allyl ethers of starch, and 1,2,3-trichloropropane; pharmaceuticals; polymers, plastics, and resins; perfumes; and insecticides

—Use of allyl chloride as a catalyst and modifier in the production of resins

—Use of allyl chloride in the production of barbiturates and hypnotic agents

The following methods are effective in controlling worker exposures to allyl chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to allyl chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, liver, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to allyl chloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic eye, respiratory, liver, or kidney abnormalities.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to allyl chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of allyl chloride on the eyes, liver, kidneys, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

No biological monitoring test acceptable for routine use has yet been developed for allyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to allyl chloride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne allyl chloride is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. The sample is then treated either with benzene or a mixture of carbon disulfide/dimethylformamide (99:1) to extract the allyl chloride. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method No. 1000 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If allyl chloride contacts their skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with allyl chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of allyl chloride, particularly its potential to be irritating to and absorbed by the skin.

A worker who handles allyl chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where allyl chloride or a solution containing allyl chloride is handled, processed, or stored.

STORAGE

Allyl chloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet OSHA requirements for Class IB flammable liquids [29 CFR 1910.106]. Containers of allyl chloride should be protected from physical damage and should be separated from incompatible chemicals, heat, sparks, and open flame. To prevent static sparks, metal containers and equipment used to transfer allyl chloride must be grounded and bonded. Because empty containers may still hold allyl chloride residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving allyl chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors, but do not use water spray to prevent ignition in closed spaces.

6. Prohibit contact with the material unless personnel are wearing fully effective personal protective equipment.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. Dike far ahead of large liquid spills for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether these requirements have been changed.

- **Emergency planning requirements**

Allyl chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a chemical release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for allyl chloride is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of allyl chloride per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of allyl chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although allyl chloride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of allyl chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, face shields, aprons, boots, and body-covering clothing) should be worn to prevent skin contact with allyl chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyvinyl alcohol and Teflon® have been tested against permeation by allyl chloride and have demonstrated breakthrough times of 1 to 4 hr. Butyl rubber, natural rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by allyl chloride.

If allyl chloride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, gas-tight goggles, or face shields should be worn during operations in which allyl chloride might contact the eyes (e.g., through splashes of solution); face shields alone, however, are not adequate for eye protection. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with allyl chloride. Contact lenses should not be worn if the potential exists for allyl chloride exposure.

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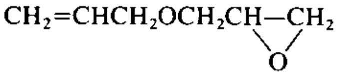
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about allyl glycidyl ether (AGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{10}O_2$
- **Structure:**



$CH_2{=}CHCH_2OCH_2CH{-}CH_2$ (O bridging CH and CH_2)

- **Synonyms:** AGE; allyl 2,3-epoxypropyl ether; 1-(allyloxy)-2,3-epoxypropane; ((2-propenyloxy)methyl)-oxirane
- **Identifiers:** CAS 106-92-3; RTECS RR0875000; DOT 2219, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a sweet odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.16
2. Boiling point (at 760 mmHg): 154°C (309°F)
3. Specific gravity (water = 1): 0.97
4. Vapor density (air = 1 at boiling point of AGE): 3.32
5. Melting point: -100°C (-148°F)
6. Vapor pressure at 25°C (77°F): 4.7 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 14.1
8. Saturation concentration in air (approximate) at 25°C (77°F): 0.62% (6,200 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. AGE should not be exposed to light or air because explosive peroxides may be formed.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving AGE.
3. Caution: AGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 57.2°C (135°F) (open cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class II Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

1. Odor threshold: 10 ppm
2. Evaluation of warning properties for respirator selection: Because of the lack of odor or irritant effects at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), AGE is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for AGE is 10 parts of AGE per million parts of air (ppm) [45 milligrams of AGE per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 9.6 ppm (45 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m³) (Skin) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 10 ppm (44 mg/m³) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes (Table 1).

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Table 1.—Occupational exposure limits for allyl glycidyl ether

	Exposure limits	
	ppm	mg/m^3
OSHA PEL ceiling	10	45
NIOSH REL ceiling (15 min)	9.6	45
ACGIH TLV® TWA (Skin)*	5	22
STEL (Skin)	10	44

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

AGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: In mice and rats, acute inhalation or oral administration of AGE caused tearing, nasal discharge, dyspnea (breathing difficulty), narcosis, and death (due to pulmonary edema and central nervous system depression); acute intramuscular injection in rats produced testicular degeneration and toxic effects on the hematopoietic (blood-cell-forming) systems, including decreased leukocyte counts and atrophy of lymphoid tissue. Subchronic inhalation of AGE by rats caused central nervous system depression, reduction in weight gain, corneal opacity, pneumonia, emphysema, and enlarged adrenal glands. AGE was mutagenic in bacterial test systems.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to AGE can cause moderate irritation of the skin and severe irritation of the eyes and respiratory tract.
2. *Long-term (chronic):* Exposure to AGE can cause dermatitis with itching, swelling, and blisters. Skin sensitization to AGE and cross sensitization with other epoxy agents can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to AGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory, nervous, hematopoietic, and reproductive systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to AGE at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such workers. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to AGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and respiratory, nervous, hematopoietic, and reproductive systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination.

Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of AGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting AGE vapors with adsorption tubes of Tenax-GC resin followed by desorption with diethyl ether and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure AGE may also be used if available. A detailed sampling and analytical method for AGE may be found in the *NIOSH Manual of Analytical Methods* (method number S346).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with AGE.

Workers should be provided with and required to use splash-proof safety goggles where AGE may come in contact with the eyes.

SANITATION

Clothing which becomes contaminated with AGE should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of AGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of AGE's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with AGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle AGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to AGE may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for allyl glycidyl ether

Operations	Controls
During use as a reactive diluent in formulation of epoxy resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a copolymer for vulcanization of rubber, surface coatings, and epoxy resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to AGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If AGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to AGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If AGE gets on the skin, wash it immediately with soap and water. If AGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty.

Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If AGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing AGE, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from AGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing AGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. AGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing AGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for allyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 96 ppm	Any supplied-air respirator Any self-contained breathing apparatus Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 240 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection) Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 270 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection) Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Planned or emergency entry into environments containing unknown concentrations or levels above 270 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 9.6 ppm (45 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL PROPYL DISULFIDE

INTRODUCTION

This guideline summarizes pertinent information about allyl propyl disulfide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}S_2$

- **Structure**

$CH_2{=}CHCH_2S_2C_3H_7$

- **Synonyms**

2-Propenyl propyl disulfide; onion oil; 4,5-dithia-1-octene; propyl allyl disulfide

- **Identifiers**

1. CAS No.: 2179-59-1
2. RTECS No.: JO0350000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Allyl propyl disulfide is a pale yellow, combustible liquid with a strong, pungent, irritating odor. It is the chief volatile constituent of onion oil.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 148.3
2. Boiling point (13 mm Hg): 78° to 80°C (172.4° to 176°F)
3. Specific gravity (water = 1): 0.93 at 15°C (59°F)
4. Vapor density: (air = 1 at boiling point of allyl propyl disulfide) 5.12
5. Melting point: Solidifies at −15°C (5°F)
6. Vapor pressure at 20°C (68°F): Data not available; however, this substance is known to be volatile.
7. Solubility: Insoluble in water; soluble in ether, carbon disulfide, and chloroform
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of allyl propyl disulfide with oxidizers.
3. Hazardous decomposition products: Toxic gases (such as sulfur oxides) may be released in a fire involving allyl propyl disulfide.
4. Special precautions: None known

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to allyl propyl disulfide. Other sources rate allyl propyl disulfide as a moderate fire hazard.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use foam, carbon dioxide, or dry chemical to fight fires involving allyl propyl disulfide. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

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Occupational Safety and Health Administration

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for allyl propyl disulfide is 2 ppm (12 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 3 ppm (18 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (12 mg/m^3) as an 8-hr TWA and 3 ppm (18 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned allyl propyl disulfide a threshold limit value (TLV) of 2 ppm (12 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL *of 3 ppm (18 mg/m^3) for periods not to exceed 15 min* [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye, nose, and upper respiratory tract irritation associated with exposure to allyl propyl disulfide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to allyl propyl disulfide can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: No studies are available on the toxicity of allyl propyl disulfide in animals.

2. *Effects on Humans*: Allyl propyl disulfide irritates the eyes, nose, throat, and mucous membranes [Proctor et al. 1988]. Allyl propyl disulfide is reported to cause lacrimation at concentrations of 2 to 3 ppm and above [Grant 1986]. Workers in an onion dehydration plant who were exposed to allyl propyl disulfide at 3.4 ppm experienced eye, nose, and throat irritation [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to allyl propyl disulfide can cause tearing eyes, runny nose, and throat irritation.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to allyl propyl disulfide have been reported.

- **Emergency procedures**

[redacted]

Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to the liquid or vapors, mists, or aerosols of allyl propyl disulfide. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve allyl propyl disulfide and may result in worker exposures to this substance:

—Slicing of onions

The following methods are effective in controlling worker exposures to allyl propyl disulfide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to allyl propyl disulfide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to allyl propyl disulfide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to allyl propyl disulfide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of allyl propyl disulfide on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for allyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne allyl propyl disulfide is determined by using a Chromosorb 106 tube (100/50-mg sections, 60/80 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with trichloroethylene to extract the allyl propyl disulfide. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.09 and is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If allyl propyl disulfide contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with allyl propyl disulfide should be removed.

A worker who handles allyl propyl disulfide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where allyl propyl disulfide is handled, processed, or stored.

STORAGE

Allyl propyl disulfide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of allyl propyl disulfide should be protected from physical damage and should be stored separately from oxidizers, heat, sparks, and open flame. Because containers that formerly contained allyl propyl disulfide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving allyl propyl disulfide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate the area of the spill or leak.
4. Absorb spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Allyl propyl disulfide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [40 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of allyl propyl disulfide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of allyl propyl disulfide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although allyl propyl disulfide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of allyl propyl disulfide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Safety glasses, goggles, or face shields should be worn during operations in which allyl propyl disulfide might contact the eyes (e.g., through splashes of solution).

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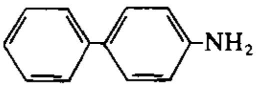
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
4-AMINODIPHENYL
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 4-aminodiphenyl for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_{11}N$
- **Structure:**



- **Synonyms:** 4-ADP; p-aminodiphenyl; 4-aminobiphenyl; 4-biphenylamine; (1,1′-biphenyl)-4-amine; diphenylamine; p-phenylaniline; xenylamine
- **Identifiers:** CAS 92-67-1; RTECS DU8925000; DOT not assigned
- **Appearance and odor:** Colorless crystals with a floral odor which turn purple on contact with air

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 169.24
2. Boiling point (at 760 mmHg): 302 °C (575.6 °F)
3. Specific gravity (water = 1): 1.160
4. Vapor density (air = 1 at boiling point of 4-aminodiphenyl): 5.8
5. Melting point: 53 °C (177 °F)
6. Solubility in water, g/100 g water at 25 °C (77 °F): 0.18

- **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 4-aminodiphenyl.

- **Flammability**

1. Flash point: 152.7 °C (307 °F) (closed cup)
2. Autoignition temperature: 635 °C (1,175 °F)
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Combustible solid, Flammability Rating 1 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 4-aminodiphenyl; however, the OSHA standard requires implementation of stringent controls wherever 4-aminodiphenyl or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-aminodiphenyl are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1011, 4-Aminodiphenyl. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 4-aminodiphenyl as an A1 carcinogen (confirmed human carcinogen) (Skin). The "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. ACGIH recommends that virtually no exposure or contact by any route (i.e., respiratory, skin, or oral, as detected by the most sensitive methods) be permitted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

4-Aminodiphenyl may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* In mice, subchronic or chronic subcutaneous injection or oral administration of 4-aminodiphenyl produced cancers of the liver, bladder, or mammary glands. Chronic oral administration of 4-aminodiphenyl to dogs caused salivation, loss of body weight, blood in the urine, and bladder cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans:* Chronic exposure of workers to 4-aminodiphenyl has been associated with an increased incidence of bladder cancer.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 4-aminodiphenyl can cause headache, lethargy, urinary tract burning, blood in the urine, and bluish discoloration of the skin and mucous membranes (due to methemoglobinemia).
2. *Long-term (chronic):* Exposure to 4-aminodiphenyl can cause blood and pus in urine and frequent, painful urination.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 4-aminodiphenyl, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 4-aminodiphenyl. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 4-aminodiphenyl. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The physician should consider use of a test which characterizes internal exposure (e.g., benzidine in urine). However, this test should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 4-aminodiphenyl may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 4-aminodiphenyl dust with glass fiber filters and silica gel tubes followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-aminodiphenyl may also be used if available. A detailed sampling and analytical method for 4-aminodiphenyl may be found in the *NIOSH Manual of Analytical Methods* (method number 269).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting from a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 4-aminodiphenyl should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 4-aminodiphenyl from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-aminodiphenyl's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 4-aminodiphenyl from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1011:

Areas where 4-aminodiphenyl is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 4-aminodiphenyl, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 4-aminodiphenyl which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-aminodiphenyl into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 4-aminodiphenyl shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 4-aminodiphenyl from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-aminodiphenyl may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 4-aminodiphenyl

Operations	Controls
During use in research and laboratory facilities	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 4-aminodiphenyl, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 4-aminodiphenyl, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-aminodiphenyl gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 4-aminodiphenyl, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-aminodiphenyl gets on the skin, wash it immediately with soap and water. If 4-aminodiphenyl penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 4-aminodiphenyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, 4-aminodiphenyl may be collected and placed in an appropriate container.
4. For small quantities of liquids containing 4-aminodiphenyl, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation.
5. Large quantities of liquids containing 4-aminodiphenyl may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
6. 4-Aminodiphenyl dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of 4-aminodiphenyl are prohibited by OSHA. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 4-aminodiphenyl

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-AMINOPYRIDINE

INTRODUCTION

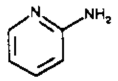
This guideline summarizes pertinent information about 2-aminopyridine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$(NH_2)C_5H_4N$

- **Structure**



- **Synonyms**

α-Aminopyridine; 1,2-dihydro-2-iminopyridine; 2-pyridylamine; o-aminopyridine; amino-2-pyridine; α-pyridinamine, 2 AP

- **Identifiers**

1. CAS No.: 504-29-0
2. RTECS No.: US1575000
3. DOT UN: 2671 55
4. DOT label: Poison

- **Appearance and odor**

2-Aminopyridine is a combustible, colorless or white, crystalline solid that has an odor described as "characteristic."

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 94.1
2. Boiling point (at 760 mm Hg): 210.6°C (411.1°F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of 2-aminopyridine): 3.2
5. Melting point: 58.1°C (136.6°F)
6. Vapor pressure at 25°C (77°F): 0.8 mm Hg
7. Solubility: Soluble in water, alcohol, benzene, ether, and acetone
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame
2. Incompatibilities: Fires and explosions may result from contact of 2-aminopyridine with strong oxidizers, strong acids, or sodium nitrate.
3. Thermal decomposition products: Toxic gases (such as oxides of nitrogen, carbon dioxide, and carbon monoxide) may be released when 2-aminopyridine burns or is heated to decomposition.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to 2-aminopyridine; other sources rate 2-aminopyridine as a moderate fire hazard.

1. Flash point: 68°C (154°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available

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4. Extinguishant: Use dry chemical, carbon dioxide, or alcohol foam to extinguish fires involving 2-aminopyridine. Do not use a solid stream of water because the stream will scatter and spread the fire. However, water spray may be used to cool fire-exposed containers.

Fires involving 2-aminopyridine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of 2-aminopyridine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving 2-aminopyridine. Chemical protective clothing that is specifically recommended for 2-aminopyridine may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by 2-aminopyridine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-aminopyridine is 0.5 part per million (ppm) parts of air (2 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 ppm (2 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-aminopyridine a threshold limit value (TLV) of 0.5 ppm (2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of systemic poisoning associated with exposure to 2-aminopyridine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-aminopyridine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: 2-Aminopyridine is a dermally absorbed, central nervous system stimulant and convulsant in animals. When instilled into the eyes of rabbits, 2-aminopyridine causes only mild, reversible injury [Grant 1986]. 2-Aminopyridine is rapidly absorbed through the skin and has caused convulsions and death in guinea pigs exposed by this route [Clayton and Clayton 1981]. The acute dermal LD_{50} in guinea pigs is 0.5 ml/kg (approximately 500 mg/kg) [Clayton and Clayton 1981]. The acute oral LD_{50} is 50 mg/kg in mice and 200 mg/kg in rats. Acutely poisoned animals exhibit tremors, excitement, seizures, and tetany before death from respiratory failure [Clayton and Clayton 1981]. 2-Aminopyridine is nonmutagenic in *Salmonella typhimurium* [NLM 1992].

2. *Effects on Humans*: Intoxication from 2-aminopyridine can occur from inhalation of the dust or vapor or from skin absorption following direct contact. 2-Aminopyridine is a convulsant in humans and is moderately irritating to the skin and eyes [Clayton and Clayton 1981]. The lowest concentration and duration of exposure reported to be toxic in humans is 5 ppm for 5 hr; the toxic effects caused by this exposure include confusion and convulsions [NIOSH 1991]. A worker who was milling 2-aminopyridine developed high blood pressure, headache, nausea, and flushing of the extremities; subsequent air sampling demonstrated a level of 5.2 ppm; this worker had recovered completely by the following day [Clayton and Clayton 1981]. A chemical operator who continued to work for 1½ hr in clothing contaminated with 2-aminopyridine developed headache, difficult breathing, dizziness, and convulsions and died from respiratory failure [Clayton and Clayton 1981]. He may also have absorbed this substance through his skin [ACGIH 1991a]. Ingestion of as little as 60 mg in adult humans has resulted in severe poisoning, which included such signs and symptoms as: profuse sweating, burning of throat, weakness, nausea, disorientation, dizziness, thirst, ocular paresthesias, psychoticlike behavior, tremors, dyspnea, and convulsions [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to 2-aminopyridine can cause irritation, headache, dizziness, nausea, flushing of the extremities, elevated blood pressure, weakness, difficult breathing, confusion, ocular paresthesias, seizures, and stupor. In severe poisoning, exposure to this substance may cause respiratory failure and death.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to 2-aminopyridine have been reported.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Irritation may result! ***Immediately*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: 2-Aminopyridine can cause skin irritation and can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If respirable 2-aminopyridine is inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to swab particulates from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if 2-aminopyridine or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 2-aminopyridine and may result in worker exposures to this substance:

—Manufacture of pharmaceuticals, especially antihistamines

—Manufacture of hair dyes and other dyes

—Use of 2-aminopyridine in chemical synthesis

The following methods are effective in controlling worker exposures to 2-aminopyridine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-aminopyridine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous and respiratory systems. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-aminopyridine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history or findings consistent with seizure or other central nervous system disorders or chronic respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-aminopyridine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-aminopyridine on the central nervous and respiratory systems. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-aminopyridine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne 2-aminopyridine is determined by using two Tenax-GC tubes in series (the first tube contains a single 35-mg section and the second tube contains a single 17-mg section; both sections are 35/60 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 12 liters is collected. The sample is then analyzed by gas chromatography using a flame ionization detector. This method is included in the OSHA Computerized Information System [OSHA 1986]. NIOSH has a similar method for analyzing 2-aminopyridine (Method S158) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Because 2-aminopyridine can be absorbed through the skin in lethal amounts, workers should immediately remove any contaminated clothing and wash thoroughly with soap and water any areas of the skin that have come in contact with this substance.

Clothing and shoes contaminated with 2-aminopyridine should be removed immediately and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of 2-aminopyridine, particularly its potential for being absorbed through the skin in lethal amounts.

A worker who handles 2-aminopyridine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where 2-aminopyridine is handled, processed, or stored.

STORAGE

2-Aminopyridine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical service in storage areas should be of explosionproof design. Containers of

2-aminopyridine should be protected from physical damage and should be stored separately from oxidizing agents, strong acids, sodium nitrate, heat, sparks, and open flame. Because empty containers may contain 2-aminopyridine residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-aminopyridine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Provide maximum explosionproof ventilation.
5. Use nonsparking tools during cleanup.
6. Carefully collect solid material and place it in a covered container for disposal.
7. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2-Aminopyridine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-aminopyridine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-aminopyridine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although 2-aminopyridine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-aminopyridine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with 2-aminopyridine. Gloves, aprons, boots, and chemical-protective suits should be worn when workers are handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-aminopyridine permeation; however, butyl rubber has been tested against chemically similar materials (pyridines) and has demonstrated good-to-excellent resistance. Since specific test data are not available for 2-aminopyridine, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-aminopyridine.

If 2-aminopyridine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-aminopyridine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-aminopyridine. Contact lenses should not be worn if the potential exists for 2-aminopyridine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMITROLE

INTRODUCTION

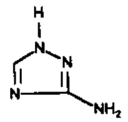
This guideline summarizes pertinent information about amitrole for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_2H_4N_4$

- **Structure**



- **Synonyms**

3-Amino-s-triazole; 2-amino-1,3,4-triazole; 3AT; ATA; aminotriazole; 3-amino-1H-1,2,4-triazole; Amitril; Amizol; Cytrol; Weedazol; Azaplant; Azolan; Diurol; Domatol; El-masil; Emisol; Fenamine; Kleer-Lot; Orga-414; Radoxone TL; X-All Liquid; Fenavar; Ramizol; Vorox

- **Identifiers**

1. CAS No.: 61-82-5
2. RTECS No.: XZ3850000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Amitrole is a nonflammable, colorless-to-white, crystalline solid that is odorless when pure. The use of amitrole on food crops is now banned in the United States; however, this substance is still imported for use as a specialty herbicide (e.g., brush killer) and as a preharvest and postharvest herbicide on selected crops.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 84.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.14 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 159°C (318.2°F)
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Soluble in water, alcohol, and chloroform; sparingly soluble in ethyl acetate; insoluble in acetone, diesel oil, ether, and kerosene
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and light
2. Incompatibilities: Amitrole in aqueous solution is neutral, but the compound acts as a weak base to form salts in contact with acids. This substance is also mildly corrosive to iron, aluminum, copper, and copper alloys.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving amitrole.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to amitrole; this substance is not flammable.

1. Flash point: Not applicable

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2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing, including a self-contained breathing apparatus, when fighting fires involving amitrole.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for amitrole is 0.2 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as an 8-hr TWA. NIOSH has also recommended that amitrole be considered a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned amitrole a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The OSHA and NIOSH limits are based on the risk of cancer associated with exposure to amitrole, and the ACGIH limit is based on the risk of systemic and reproductive (fetotoxicity) effects associated with exposure to amitrole.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to amitrole can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Amitrole is a potent antithyroid agent and an animal carcinogen. Amitrole is slightly irritating to the eyes and skin of exposed rabbits [ACGIH 1991a]. Acute dermal exposure of rats and rabbits to 10,000 mg/kg did not induce toxicity. Exposure of rats to 439 mg/m^3 for 4 hr did not induce eye or respiratory tract irritation or toxicity [ACGIH 1991a]. The oral LD_{50} for mice and rats ranges from 11,000 to 14,000 mg/kg [ACGIH 1991a; Clayton and Clayton 1982]; however, a 25,000-mg/kg LD_{50} has also been cited for rats [ACGIH 1991a; NIOSH 1991]. When administered to young rabbits (dose and route not specified), amitrole produced cataracts and reduced the catalase activity within the lens [Grant 1986]. A number of subchronic studies via oral routes of administration have established the thyroid as the primary target organ of amitrole toxicity. In rats, the no observable effect level (NOEL) based on normal iodine 131 uptake was 0.5 ppm amitrole in the diet consumed during 13 weeks of exposure. Decreased thyroid function required 1.0 ppm in the diet for 29 days. Induction of increased thyroid weights required a minimum of 10 ppm in the diet for 13 weeks [ACGIH 1991a]. In addition, rats fed amitrole in drinking water (12 to 14 mg/day) developed goiter and showed histologic evidence of thyroid pathology at autopsy [Clayton and Clayton 1981]. Dietary exposure of breeding pairs of rats to amitrole caused reduced growth and viability of offspring [IARC 1986], and oral administration to pregnant mice caused fetotoxicity [NLM 1991]. In vitro mammalian test systems indicate that amitrole is also mutagenic [NIOSH 1991]. Amitrole has been tested for carcinogenicity in mice (by oral administration, skin application, and transplacental exposure), in rats (by oral and subcutaneous administration), and in hamsters (by oral administration). Orally, this substance produced thyroid tumors, liver carcinomas, and benign and malignant liver tumors in mice of both sexes; it also caused benign and malignant (adenocarcinomas) thyroid tumors in rats of both sexes, and benign pituitary tumors in female rats [IARC 1987]. On the basis of these studies, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of amitrole in animals is sufficient [IARC 1987].

2. *Effects on Humans*: Amitrole is a thyroid toxin in humans. On the basis of effects seen in animals, this substance is also a potential occupational carcinogen. There have been no reports of signs or symptoms in exposed individuals, but extrapolations from animal data suggest that dyspnea, muscle spasms, fasciculations, ataxia, anorexia, salivation, and increased body temperature could occur [NLM 1991]. A single oral dose of 100 mg of amitrole given to volunteers inhibited thyroid iodine uptake for 24 hr after administration; the volunteers included healthy persons as well as individuals with hyperthyroidism [ACGIH 1991a]. Ingestion of 20 mg/kg of a commercial preparation (30% amitrole) by a 39-year-old woman did not induce signs or symptoms of toxicity [NLM 1991]. A small cohort study of Swedish railroad workers exposed for 45 days or more to amitrole, other pesticides, and organic and inorganic chemicals revealed an excess number of deaths from cancer. A subgroup of these workers exposed both to amitrole and chlorophenoxy herbicides had an increase in cancer mortality that was statistically significant; however, in the subgroup exposed primarily to amitrole alone, no

significant excess was seen [IARC 1987]. On the basis of this study, IARC has concluded that the evidence for the carcinogenicity of amitrole in humans is inadequate [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Other than mild irritation, no signs or symptoms of acute exposure to amitrole have been reported.

2. *Chronic exposure*: On the basis of effects seen in animals, the signs and symptoms of chronic exposure to amitrole could include dyspnea, muscle spasms, ataxia, anorexia, salivation, and increased body temperature; or lassitude, skin dryness, depression, and other effects indicative of thyroid function suppression.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of amitrole. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of amitrole are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if amitrole or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses involve amitrole and may result in worker exposures to this substance:

—Use in the formulation of herbicides

—Use as a herbicide for hardwood nursery stock, aquatic weeds, and nonselective weed control along highways and railroads

—Use as a cotton defoliant and as a reagent in photography

—Use as a herbicide on poison ivy and poison oak

—Use as a herbicide on food crops (now banned in the United States)

The following methods are effective in controlling worker exposures to amitrole, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to amitrole, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the thyroid gland, and they should include measurement of the individual's pre-exposure level of thyroid activity.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to amitrole at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the thyroid gland.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to amitrole exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of amitrole on the thyroid gland. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for amitrole.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to amitrole may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne amitrole is determined by using a midget impinger containing 10 ml of distilled water. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. The limit of detection for this procedure is 0.004 mg/m^3. This method is described in the OSHA Computerized Information System [OSHA 1988] and in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If amitrole contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with amitrole should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of amitrole.

A worker who handles amitrole should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where amitrole or a solution containing amitrole is handled, processed, or stored.

STORAGE

Amitrole should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of amitrole should be protected from physical damage and should be stored separately from acids, heat, and light. Because containers that formerly contained amitrole may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving amitrole, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
3. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
4. For large liquid spills, build dikes far ahead of the spill to contain the amitrole for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Amitrole is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State or local authorities.

The reportable quantity for amitrole is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of amitrole emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Amitrole is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U011. This substance has been banned from land disposal and may be treated by incineration. Amitrole also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of amitrole exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's *respiratory protection standard* [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any possibility of skin contact with amitrole. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to amitrole permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to amitrole.

If amitrole is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which amitrole might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with amitrole. Contact lenses should not be worn if the potential exists for amitrole exposure.

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Occupational Health Guideline for Ammonia

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: NH_3
- Synonyms: Anhydrous ammonia
- Appearance and odor: Colorless gas with a penetrating, pungent, suffocating odor; it can be a liquid under pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ammonia is 50 parts of ammonia per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of ammonia per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 50 ppm ammonia (35 mg/m^3) averaged over a five-minute period. The NIOSH Criteria Document for Ammonia should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ammonia can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Ammonia is a severe irritant of the eyes, respiratory tract, and skin. It may cause burning and tearing of the eyes, runny nose, coughing, chest pain, cessation of respiration, and death. It may cause severe breathing difficulties which may be delayed in onset. Exposure of the eyes to high gas concentrations may produce temporary blindness and severe eye damage. Exposure of the skin to high concentrations of the gas may cause burning and blistering of the skin. Contact with liquid ammonia may produce severe eye and skin burns. Contact of the eyes, nose, throat, and skin with solutions of ammonia may produce severe burns.

2. Long-term Exposure: Repeated exposure to ammonia gas may cause chronic irritation of the eyes and upper respiratory tract.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ammonia.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ammonia at potentially hazardous levels:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ammonia causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ammonia is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examinations: The above medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Ammonia vapor is a severe irritant of the eyes, especially the cornea, the respiratory tract, and skin. Inhalation of concentrations of 2500 to 6500 ppm causes dyspnea,

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bronchospasm, chest pain and pulmonary edema which may be fatal; production of pink frothy sputum often occurs. Consequences can include bronchitis or pneumonia; some residual reduction in pulmonary function has been reported. In a human experimental study which exposed 10 subjects to various vapor concentrations for 5 minutes, 134 ppm caused irritation of the eyes, nose, and throat in most subjects and 1 person complained of chest irritation; at 72 ppm, several reported the same symptoms; at 50 ppm, 2 reported nasal dryness and at 32 ppm only 1 reported nasal dryness. In a survey of 8 workers in a blueprint shop, ammonia concentrations of 4 to 29 ppm caused "barely noticeable" to "moderate" eye irritation; no respiratory irritation was reported. Tolerance to usually irritating concentrations of ammonia may be acquired by adaptation, a phenomenon frequently observed among workers who became inured to the effects of exposure; no data are available on concentrations that are irritating to workers who are regularly exposed to ammonia and who presumably have a higher irritation threshold. Liquid anhydrous ammonia in contact with the eyes may cause serious eye injury or blindness; on the skin it causes first- and second-degree burns which are often severe, and if extensive, may be fatal. Vapor concentrations of 10,000 ppm are mildly irritating to the moist skin, while 30,000 ppm or greater causes a stinging sensation and may produce skin burns and vesiculation. Increased cancer has been reported in workers exposed to high levels of ammonia and amines, although lack of details makes evaluation difficult.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 17
2. Boiling point (760 mm Hg): −33.4 C (-28 F)
3. Specific gravity (water = 1): Liquid 0.67 at boiling point
4. Vapor density (air = 1 at boiling point of ammonia): 0.6
5. Melting point: −77.7 C (-108 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 51
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with calcium, hypochlorite bleaches, gold, mercury, and silver may form highly explosive products. Contact with halogens may cause violent spattering.
3. Hazardous decomposition products: None.
4. Special precautions: Liquid ammonia will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 651 C (1204 F)
3. Flammable limits in air, % by volume: Lower: 16; Upper: 25
4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "ammonia is a colorless gas with a characteristic odor detectable at 1 to 5 ppm."
2. Eye Irritation Level: Grant states that "ammonia is slightly irritant to human eyes at a concentration of 140 ppm in air and immediately irritating at 700 ppm."
3. Other Information: The *Hygienic Guide* states that "irritation of the respiratory tract in workers inhaling 100 ppm has been found, but 55 ppm was unobjectionable."
4. Evaluation of Warning Properties: Because of its low thresholds of odor and irritation, ammonia is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of ammonia. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ammonia may be used. An analytical method for ammonia is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid anhydrous ammonia or aqueous solutions of ammonia containing more than 10% by weight of ammonia and to prevent the skin from becoming frozen from contact with vessels containing liquid anhydrous ammonia.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing 10% or less by weight of ammonia.
- Where there is any possibility of exposure of an employee's body to liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight should be removed immediately and not reworn until the ammonia is removed from the clothing.
- Non-impervious clothing which becomes wet with solutions containing 10% ammonia by weight or less should be removed promptly and not reworn until the ammonia is removed from the clothing.
- Clothing wet with liquid anhydrous ammonia or aqueous solutions of ammonia should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ammonia from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ammonia, the person performing the operation should be informed of ammonia's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where solutions containing 10% ammonia by weight or less may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid anhydrous ammonia or solutions containing more than 10% ammonia by weight should be immediately washed or showered to remove any ammonia.
- Skin that becomes wet with solutions containing 10% ammonia by weight or less should be promptly washed or showered to remove any ammonia.
- Employees who handle liquid anhydrous ammonia or aqueous solutions of ammonia should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ammonia may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical in manufacture of fertilizers, as solvent in manufacture of textiles, leather, and pulp and paper processing; as a stabilizer in rubber manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in organic and inorganic synthesis of nitric acid, urea, plastics, fibers, synthetic resins, pharmaceuticals, pesticides, explosives, rocket fuels, cyanides, amides, dyestuffs, amines, flame retardants, and household cleaners	Process enclosure; local exhaust ventilation; personal protective equipment
Use in mining/ metallurgy ore extraction and purification, treatment of scrap metal, annealing, atomic hydrogen welding, electronics, nitriding steel	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in petroleum refining as a neutralizing agent; manufacture and recovery of cracking catalysts; and in dewaxing of lubrication oils	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a refrigerant in food installations, production of ice, cold-storage, food lockers, deicing	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during blueprinting and photography, electroplating, and as a laboratory reagent	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid anhydrous ammonia, solutions containing ammonia, or high concentrations of ammonia gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid anhydrous ammonia, strong solutions of ammonia, or high concentrations of ammonia gas get on the skin, immediately flush the contaminated skin with water. If liquid anhydrous ammonia, strong solutions containing ammonia, or high concentrations of ammonia gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ammonia, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ammonia has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the ammonia. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ammonia is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in liquid form, allow to vaporize.

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RESPIRATORY PROTECTION FOR AMMONIA

Condition	**Minimum Respiratory Protection* Required Above 50 ppm**
Gas Concentraton	
100 ppm or less	Any chemical cartridge respirator with an ammonia cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
300 ppm or less	A chemical cartridge respirator with a full facepiece and an ammonia cartridge(s).
500 ppm or less	A gas mask with a chin-style or a front- or back-mounted ammonia canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against ammonia. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ammonia; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMMONIA

INTRODUCTION

This guideline summarizes pertinent information about ammonia for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

NH_3

- **Structure**

NH_3

- **Synonyms**

Anhydrous ammonia, ammonia gas, Am-fol, Nitro-sil, aqua ammonia, spirit of hartshorn

- **Identifiers**

1. CAS No.: 7664-41-7
2. RTECS No.: BO0875000
3. DOT UN: 1005 15 (anhydrous); 2073 15 (solutions containing more than 44% ammonia); 2672 60 (solutions containing 12% to 44% ammonia)
4. DOT labels: Poison Gas, Nonflammable Gas

- **Appearance and odor**

At room temperature, ammonia is a colorless, flammable gas; it is shipped as a liquid under its own vapor pressure. This substance has a penetrating and pungent odor. The odor threshold is reported to be 5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 17.0
2. Boiling point (at 760 mm Hg): −33.4°C (−28°F)
3. Specific gravity: 0.77 at 0°C (32°F)
4. Vapor density (air = 1 at boiling point of ammonia): 0.6
5. Melting point: −77.7°C (−107.8°F)
6. Vapor pressure at 20°C (68°F): 8,500 mm Hg
7. Solubility: Very soluble in water, alcohol, ether, and chloroform
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Under certain conditions, mixtures of ammonia and air will explode when ignited.
2. Incompatibilities: Fires and explosions may result from contact of ammonia with trimethylammonium amide, 1-chloro-2,4-dinitrobenzene, o-chloronitrobenzene, platinum, trioxygen difluoride, selenium difluoride dioxide, boron halides, acids, mercury, chlorine, iodine, bromine, hypochlorites, or chlorine bleach.
3. Hazardous decomposition products: Toxic gases (such as hydrogen gas, nitrogen gas, and nitrous oxides) may be released when ammonia decomposes.
4. Special precautions: Liquid ammonia attacks some coatings and some forms of plastic and rubber; this substance should not be allowed to contact copper, brass, bronze, or galvanized steel.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to ammonia.

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1. Flash point: Not applicable (ammonia is a gas at room temperature).

2. Autoignition temperature: 651°C (1,204°F)

3. Flammable limits in air (% by volume): Lower, 16; upper, 25.

4. Extinguishant: Use water spray or fog.

Fires involving ammonia should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and should ventilate closed spaces before entering. Containers of ammonia may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Do not get water inside the container. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Because ammonia is highly soluble in water, dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ammonia. Firefighters' protective clothing may not provide protection against permeation by ammonia.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ammonia is 35 ppm (27 mg/m^3) as a 15-min short-term exposure limit (STEL) [29 CFR 1910.1000, Table Z-1-A]. A STEL is a 15-min time-weighted average (TWA) exposure which should not be exceeded at any time during the workday.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for ammonia of 25 ppm (17 mg/m^3) as an 8-hr TWA and 35 ppm as a STEL [NIOSH 1992a].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ammonia a threshold limit value (TLV) of 25 ppm (17 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek; a STEL of 35 ppm (24 mg/m^3) has been established for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye irritation and respiratory effects associated with exposure to ammonia. OSHA did not find it necessary to establish a TWA to protect against chronic effects. OSHA concluded that a STEL would protect against the substance's irritant effects.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ammonia can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Ammonia is a severe irritant of the eyes, respiratory tract, and skin. Liquified ammonia can induce freezing, burns, and corrosion of tissues. Exposure of guinea pigs to 5,000 to 6,000 ppm for 30 to 120 min induced blindness [AIHA 1988]. The approximate 1-hr LC_{50} for cats and rabbits was 9,900 ppm. This concentration induced severe bronchiolar damage, alveolar congestion, edema atelectasis, hemorrhage, and emphysema in the animals that died [NLM 1991]. The 4-hr LC_{50} in rats is 2,000 ppm, and the oral LD_{50} is 350 mg/kg [NIOSH 1992b]. In mice, the RD_{50} (the concentration capable of reducing respiratory rate by 50%) was approximately 300 ppm. Continued exposure for 6 hr/day for 5 days produced nasal lesions including hypertrophy, hyperplasia, epithelial erosion, ulceration, and necrosis [NLM 1991]. Continuous exposure to ammonia for several weeks at 658 ppm produced marked eye irritation in dogs and rabbits and corneal opacity in rabbits [Grant 1986]. Rats similarly exposed developed interstitial pneumonitis with calcification of the bronchi and renal tubules, epithelial proliferation of the renal tubules, myocardial fibrosis, and fatty liver [NLM 1991]. Rats, guinea pigs, dogs, rabbits, and monkeys exposed to 1,100 ppm for 8 hr/day, 5 days/week for 6 weeks showed signs of moderate eye and nasal irritation but no signs of systemic poisoning [AIHA 1988]. Although all monkeys, dogs, and rabbits survived a continuous 90-day exposure to 680 ppm, this exposure was fatal to 13 of 15 rats and 4 of 15 guinea pigs [AIHA 1988]. No clinically significant findings were detected at autopsy in rats continuously exposed to 180 ppm for 90 days [AIHA 1988; Clayton and Clayton 1981].

2. *Effects on Humans*: Ammonia gas is severely irritating to the eyes and to the moist skin and mucous membranes of humans. In contact with the eyes, liquid anhydrous ammonia causes severe damage that may lead to blindness [Proctor et al. 1988]. When in contact with the skin, liquified ammonia can cause freezing and third-degree burns [NLM 1991; Proctor et al. 1988]. Two volunteers exposed to ammonia at approximately 24 ppm showed signs of mild nasal irritation

on clinical examination [Clayton and Clayton 1981]. Five of six volunteers exposed to 30 or 50 ppm for 10 min reported mild to moderate eye and upper respiratory tract irritation [Clayton and Clayton 1981]. At 130 ppm, however, volunteers experienced lacrimation and nose and throat irritation; one volunteer experienced pulmonary irritation [Clayton and Clayton 1981]. Exposure of humans to 500 ppm for 30 min caused changes in respiratory rate, and exposure to 1,720 ppm produced coughing in exposed individuals [AIHA 1988]. Accidental exposure to ammonia gas or the vapors of ammonia at high concentrations (approximately 2,500 to 6,500 ppm) for up to 2 hr induced chemical pneumonitis, burns (eyes, face, and mouth), severe local edema, dyspnea, progressive cyanosis, and death [Proctor et al. 1988; Clayton and Clayton 1981]. Death is normally caused by either suffocation or pulmonary edema [Clayton and Clayton 1981]. In near-lethal cases, residual effects may include visual impairment, decreased pulmonary function, and hoarseness [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Increasing ambient concentrations can cause contact irritation of the eyes and respiratory tract, tearing, hoarseness, violent coughing, painful breathing, impaired vision, severe eye damage, blindness, dyspnea, cyanosis, suffocation, and death. Direct contact with liquid anhydrous ammonia can cause frostbite and corrosion of the eyes and skin.

2. *Chronic exposure*: Exposure to ammonia can induce irritation of the eyes, nose, and upper respiratory tract, with coughing and difficult breathing.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***; if tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia persists, get medical attention as soon as possible.

2. *Skin exposure*: If frostbite has occurred, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If frostbite has ***not*** occurred, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if an ammonia solution is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of ammonia may result in worker exposures to this substance:

—Use as a soil fertilizer

—Use in the manufacture of fertilizers; as a solvent in the manufacture of textiles, leather, and pulp and paper processing; and as a stabilizer in the manufacture of rubber

—Use in organic and inorganic synthesis of nitric acid, urea, plastics, fibers, synthetic resins, pharmaceuticals, pesticides, explosives, rocket fuels, cyanides, amides, dyestuffs, amines, flame retardants, household cleaners, sulfuric acid, and alkalies

—Use in mining and metallurgy, ore extraction and purification, treatment of scrap metal, annealing, atomic hydrogen welding, electronics, and nitriding of steel

—Use in petroleum refining as a neutralizing agent, in the manufacture and recovery of cracking catalysts, and in the dewaxing of lubrication oils

—Use as a commercial refrigerant in food processing, the production of ice, cold storage, and de-icing operations

—Use as a substitute for calcium in the bisulfite pulping of wood

—Use with chlorine to purify municipal and industrial water supplies

The following methods are effective in controlling worker exposures to ammonia, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations must be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ammonia, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ammonia at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ammonia exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ammonia on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ammonia.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to ammonia may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ammonia is determined by using sulfuric-acid-impregnated carbon bead tubes (Supelco ORBO-77 tubes). Samples are collected at a maximum flow rate of 0.1 liter/min until a minimum air volume of 1.5 liters or a maximum air volume of 24 liters is collected. The samples are desorbed with deionized water and analyzed by ion chromatography. The limit of detection for this procedure is 1.5 ppm. This method is described in *OSHA Analytical Laboratory Method* ID-188 [OSHA 1988]. NIOSH has a similar method for analyzing ammonia using liquid sorbent badges and the same analytical procedure (Method 6701) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If ammonia contacts the skin, workers should immediately wash the affected areas with large quantities of water. Clothing contaminated with liquid ammonia should be removed immediately and should then be thoroughly flushed with cold water. Persons laundering contaminated clothing should be informed of the hazardous properties of ammonia, particularly its potential for skin irritation.

A worker who handles ammonia should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ammonia or a solution containing ammonia is handled, processed, or stored.

STORAGE

Ammonia should be stored in a cool, well-ventilated, fire-resistant area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers of ammonia should be protected from physical damage and should be separated from oxidizers, combustible materials, heat, sparks, and open flame. Explosion proof electrical service must be installed in storage areas. Because containers that formerly contained ammonia may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ammonia, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.

6. For small leaks, flood the area with cool water.

7. For large liquid spills, build dikes far ahead of the spill to contain the ammonia for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 500 lb or more of ammonia onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of a hazardous substance into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is equal or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ammonia is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of ammonia per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ammonia emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although ammonia is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ammonia exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves, boots, aprons, full-body suits, etc. should be worn as necessary. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against ammonia and have demonstrated good to excellent resistance: butyl rubber and Teflon®. Butyl rubber may provide more than 8 hr of resistance to permeation. Saranex® has demonstrated poor resistance to permeation by ammonia.

If ammonia is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ammonia might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ammonia.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMMONIUM CHLORIDE FUME

INTRODUCTION

This guideline summarizes pertinent information about ammonium chloride fume for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

NH_4Cl

- **Synonyms**

Amchlor fume, ammoneric fume, ammonium muriate fume, darammon fume, sal ammonia fume, salammoniac fume, salammonite fume, salmiac fume

- **Identifiers**

1. CAS No.: 12125-02-9
2. RTECS No.: BP4550000
3. DOT UN: 9085 31
4. DOT label: None

- **Appearance and odor**

Ammonium chloride is a noncombustible, white, crystalline solid. It is odorless and somewhat hygroscopic. Ammonium chloride fume is the finely divided particulate form of this substance.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 53.5
2. Boiling point (760 mm Hg): 520°C (968°F)
3. Specific gravity (water = 1): 1.52 at 25°C (77°F)
4. Vapor density: Not applicable
5. Melting point: 350°C (662°F) sublimes
6. Vapor pressure at 160.4°C (320.7°F): 1 mm Hg
7. Solubility: Soluble in water, liquid ammonia, methanol, and ethanol; practically insoluble in acetone, ether, and ethyl acetate
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Violent reactions may result from contact of ammonium chloride fume with boron trifluoride, boron pentafluoride, iodine heptafluoride, or potassium chlorate. In the presence of alkalies, ammonia is evolved; in the presence of acids, hydrogen chloride is evolved. Ammonium chloride is also incompatible with the salts of lead or silver.
3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia and hydrochloric acid) may be released in a fire involving ammonium chloride fume.
4. Special precautions: At fire temperatures, ammonium chloride fume corrodes metals.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to ammonium chloride fume. This substance is not combustible.

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1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use water spray to reduce the fumes and irritant gases produced in a fire involving ammonium chloride. For small fires, use dry chemical, Halon®, water spray, foam, or other noncombustible material suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ammonium chloride fume.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for ammonium chloride fume are 10 mg/m^3 of air as an 8-hr time-weighted average (TWA) and 20 mg/m^3 as a short-term exposure limit (STEL)—the 15-min TWA that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 as an 8-hr TWA and 20 mg/m^3 as a STEL (15-min TWA) [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ammonium chloride fume a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and 20 mg/m^3 as a STEL (15-min TWA) [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of respiratory system irritation associated with exposure to ammonium chloride fume.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to ammonium chloride fume can occur through inhalation and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Ammonium chloride is a tissue irritant and metabolic acidifying agent. Topical administration of 100 or 500 mg onto the eyes of rabbits caused severe or mild irritation, respectively [NIOSH 1991]. No animal data are available on the toxic effects of inhalation exposure to the fume of ammonium chloride. The acute oral LD_{50} in rats is 1,650 mg/kg [NIOSH 1991]. An acute lethal intravenous dose to mice induced hyperventilation, convulsions, coma, and death [NLM 1991]. During a 13-week subchronic study, 10 male rats ingested a purified diet containing 5% ammonium chloride. This metabolic acidifying agent depressed food consumption and weight. Necropsy of an animal that died during week 10 revealed hemorrhagic abdominal fluid, a blood clot in the enlarged urinary bladder, inflammation of the seminal vesicles and prostate, and haemothorax. Terminal relative kidney weights were also increased. Histopathology of selected organs demonstrated only a diffuse hyperplasia of the urinary bladders in 4 of 10 rats treated with ammonium chloride. Two males had a moderate hyperplasia, and two other males had severe hyperplasia with small papillary protrusions [NIOSH 1991; de Groot et al. 1988].

2. *Effects on Humans*: Ammonium chloride fume is a mild irritant of the eyes, nose, throat, lungs, and skin in humans. Repeated inhalation of ammonium chloride fumes (concentration unspecified) during welding also caused pulmonary sensitization in some workers [Genium 1991]. A 50-year-old woman ingested 6 g of ammonium chloride per day as a urine acidifying agent for the treatment of renal stone disease, air hunger, and profound metabolic acidosis [NLM 1991]. Ingestion of large doses of this chemical induced nausea, gastric irritation and distress, vomiting, thirst, headache, hyperventilation, progressive drowsiness, anorexia, bradycardia, mental confusion, phases of excitement, calcium-deficient tetany, tremors, hyperreflexia, and coma. Clinical chemistry analyses revealed the following adverse alterations: profound metabolic acidosis, hypokalemia, hyperchloremia, hyperglycemia, and glycosuria. EEG abnormalities have also been reported [NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to ambient ammonium chloride can cause irritation of contacted tissues. Ingestion exposure can cause nausea, gastric irritation and distress, vomiting, thirst, headache, hyperventilation, progressive drowsiness, anorexia, bradycardia, mental confusion, phases of excitement, calcium-deficient tetany, tremors, hyperreflexia, and coma.

2. *Chronic exposure*: Chronic exposure to ammonium chloride fume can cause difficult breathing, wheezing, and coughing in sensitized individuals.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of ammonium chloride may result in worker exposures to ammonium chloride fume:

—Use as a flux for coating sheet iron with zinc, in tinning, and in soldering

—Use in dry and Leclanche batteries

—Use in electroplating and welding

—Use in cleaning soldering irons

The following methods are effective in controlling worker exposures to ammonium chloride fume, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ammonium chloride fume, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ammonium chloride fume at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with allergies or with respiratory tract or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ammonium chloride fume exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ammonium chloride fume on the respiratory tract and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ammonium chloride fume.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ammonium chloride fume is determined by using a tared, low-ash polyvinyl chloride filter (5-micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing). This method has a sampling and analytical error of 0.10 and is described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985].

PERSONAL HYGIENE

If ammonium chloride fume contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with ammonium chloride fume should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of ammonium chloride fume, particularly its potential for causing irritation.

A worker who handles ammonium chloride fume should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ammonium chloride fume is generated.

RELEASES

In the event of a large release of ammonium chloride fume, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a release:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate potentially explosive atmospheres.
4. Use cleanup procedures such as vacuuming and wet mopping to minimize dust generation.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Ammonium chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for ammonium chloride fume is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ammonium chloride fume emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although ammonium chloride fume is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ammonium chloride fume exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with ammonium chloride fume. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Chlorinated polyethylene is recommended for protection against ammonium chloride.

Safety glasses, goggles, or face shields should be worn during operations in which ammonium chloride fume might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ammonium chloride fume. Contact lenses should not be worn if the potential exists for exposure to ammonium chloride fume.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMMONIUM SULFAMATE

INTRODUCTION

This guideline summarizes pertinent information about ammonium sulfamate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$NH_4SO_3NH_2$

- **Synonyms**

Ammonium amidosulfonate, ammonium amidosulphate, monoammonium sulfamate, sulfamic acid, monoammonium salt, sulfamate, Ammate, Amcide, Ammat, Amicide

- **Identifiers**

1. CAS No.: 7773-06-0
2. RTECS No.: WO6125000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Ammonium sulfamate is a white, brown-gray, or colorless crystalline noncombustible solid that is odorless.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.1
2. Boiling point (at 760 mm Hg): Decomposes at 160°C (320°F)
3. Specific gravity (water = 1): 1.77
4. Vapor density: Not applicable
5. Melting point: 131°C (268°F)
6. Vapor pressure at 20°C (68°F): Zero
7. Solubility: Highly soluble in water and liquid ammonia; moderately soluble in glycerol, glycol, and formamide; slightly soluble in ethanol
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Fires and explosions may result from contact of ammonium sulfamate with strong oxidizers, hot water, potassium, sodium, sodium nitrite, metal chlorates, or hot acid solutions.
3. Hazardous decomposition products: Toxic gases (such as nitrogen or sulfur oxides and carbon monoxide) may be released when ammonium sulfamate decomposes.
4. Special precautions: Ammonium sulfamate is corrosive to mild steel.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to ammonium sulfamate; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ammonium sulfamate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for ammonium sulfamate are 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr TWAs [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ammonium sulfamate a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of physical irritation associated with exposure to ammonium sulfamate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ammonium sulfamate can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Ammonium sulfamate has a low order of toxicity in animals. When instilled into the eyes of rabbits, a 4% solution caused no irritation [Grant 1986]. The application of 20% to 50% solutions of ammonium sulfamate to the shaved skin of rats failed to produce irritation or systemic toxicity [ACGIH 1991a]. However, rabbits dermally exposed to 15% to 30% solutions for 20 days developed slight skin reactions [NLM 1991]. The oral LD_{50} is 2,000 mg/kg for rats and 3,100 mg/kg for mice [NIOSH 1991]. Continuous feeding studies in rats have shown that chronic ingestion of high doses of ammonium sulfamate impairs growth but produces no other adverse effects [ACGIH 1991a]. Intraperitoneal injection of 0.8 g/kg ammonium sulfamate in rats produced respiratory stimulation and prostration before death occurred [Proctor et al. 1988].

2. *Effects on Humans*: Ammonium sulfamate dust can cause irritation of the eyes, skin, and mucous membranes. Few data are available on the effects of ammonium sulfamate exposure in humans. Repeated application of a 4% solution to the forearms of five volunteers did not produce irritation [Proctor et al. 1988]. Ingestion has caused gastrointestinal disturbances.

- **Signs and symptoms of exposure**

1. *Acute exposure*: The signs and symptoms of acute overexposure to ammonium sulfamate include possible irritation of the eyes and nose, cough, gastrointestinal disturbances, respiratory stimulation, prostration, and death.

2. *Chronic exposure*: No signs or symptoms of chronic ammonium sulfamate exposure have been reported.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if ammonium sulfamate is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures

(e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ammonium sulfamate and result in worker exposures to this substance:

—Application of ammonium sulfamate as a herbicide for control of woody plants

—Manufacture of fire-retardant compositions for flameproofing textiles and paper products

—Generation of nitrous oxide gas

—Manufacture of electroplating solutions

The following methods are effective in controlling worker exposures to ammonium sulfamate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ammonium sulfamate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and upper respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ammonium sulfamate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with drug allergies, aspirin intolerance, or eye, skin, or upper respiratory tract diseases; individuals using anticoagulant medications also may be at increased risk.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ammonium sulfamate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ammonium sulfamate on the eyes, skin, or upper respiratory tract or on blood clotting time. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ammonium sulfamate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ammonium sulfamate is determined by using tared, low-ash polyvinyl chloride filters (5 microns). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. This is a gravimetric field test method based on the total weight collected; therefore, the sample does not need to be submitted to the laboratory for analysis. This method is described under "Filter Weighting Procedure" in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985]. Additional information can be found in Method 348 of the *Occupational Exposure Sampling Strategy Manual* [NIOSH 1977].

PERSONAL HYGIENE

If ammonium sulfamate contacts the skin, workers should wash the affected areas with soap and water.

Clothing and shoes that are grossly contaminated with ammonium sulfamate should be removed and provisions should be made for safely removing this chemical from these articles.

A worker who handles ammonium sulfamate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ammonium sulfamate is handled, processed, or stored.

STORAGE

Ammonium sulfamate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of ammonium sulfamate should be protected from physical damage and should be separated from strong oxidizers, water, potassium, sodium, sodium nitrite, metal chlorates, hot acid solutions, heat, sparks, and open flame. Because containers that formerly contained ammonium sulfamate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving ammonium sulfamate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate atmosphere to reduce the dust concentration.
5. Cover spills with a plastic sheet or tarp to minimize spreading; use a clean shovel to place the material into a clean, dry container; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Ammonium sulfamate is not subject to EPA's emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act

(CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ammonium sulfamate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ammonium sulfamate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although ammonium sulfamate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ammonium sulfamate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with ammonium sulfamate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to ammonium sulfamate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to ammonium sulfamate.

If ammonium sulfamate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ammonium sulfamate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ammonium sulfamate. Contact lenses should not be worn if the potential exists for ammonium sulfamate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-AMYL ACETATE

INTRODUCTION

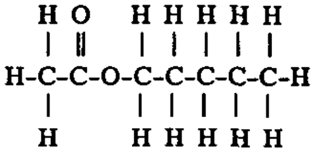
This guideline summarizes pertinent information about n-amyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CH_3COO(CH_2)_4CH_3$

- **Structure**



$$\begin{array}{ccccccccc} & H & O & & H & H & H & H & H \\ & | & \| & & | & | & | & | & | \\ H- & C- & C- & O- & C- & C- & C- & C- & C-H \\ & | & & & | & | & | & | & | \\ & H & & & H & H & H & H & H \end{array}$$

- **Synonyms**

Pentyl acetate, amyl acetic ester, pear oil, acetic acid, amyl ester, acetic acid, pentyl ester, amyl acetate, amyl acetic ether, pent-acetate, 1-pentanol acetate, primary amyl acetate

- **Identifiers**

1. CAS No.: 628-63-7
2. RTECS No.: AJ1925000
3. DOT UN: 1104 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

n-Amyl acetate is a flammable, colorless liquid with a bananalike odor. The odor threshold is reported to be 0.15 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.2
2. Boiling point (at 760 mm Hg): 149°C (300°F)
3. Specific gravity (water = 1): 0.88 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-amyl acetate): 4.5
5. Melting point: −70.5°C (−94.9°F)
6. Vapor pressure at 20°C (68°F): 4 mm Hg
7. Solubility: Slightly soluble in water, miscible with alcohol and ether
8. Evaporation rate (butyl acetate = 1): 0.42

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or flames
2. Incompatibilities: Fire and explosion may result from contact with nitrates, strong oxidizers, strong alkalies, or strong acids.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide), acrid smoke, and irritating fumes may be released when n-amyl acetate decomposes.
4. Special precautions: n-Amyl acetate can damage some plastics, rubbers, and coatings.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to n-amyl acetate.

1. Flash point: 25°C (77°F) (closed cup)
2. Autoignition temperature: 360°C (680°F)
3. Flammable limits in air (% by volume): Lower, 1.1; upper, 7.5

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4. Extinguishant: Use dry chemical, carbon dioxide, or alcohol foam to fight fires involving n-amyl acetate. Water should not be used as an extinguishant because it will spread the flames.

Fires involving n-amyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-amyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-amyl acetate. Firefighters' protective clothing may not provide protection against permeation by n-amyl acetate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-amyl acetate is 100 ppm (525 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 100 ppm (525 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-amyl acetate a threshold limit value (TLV) of 100 ppm (525 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation of the eyes and respiratory passages associated with exposure to n-amyl acetate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to n-amyl acetate can occur through inhalation, ingestion, or contact with the skin, eyes, and mucous membranes. n-Amyl acetate can also be absorbed slowly through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: n-Amyl acetate is an irritant of the eyes, skin, and respiratory tract in animals. When instilled into the eyes of rabbits, n-amyl acetate liquid causes mild and reversible corneal epithelial injury [Grant 1986]. When it contacts the skin, n-amyl acetate causes defatting [AIHA 1978]. The oral LD_{50} in rats is 6,500 mg/kg [NIOSH 1991]. In rabbits, the LD_{50} in a 24-hr covered skin penetration test is greater than 20 ml/kg [AIHA 1978]. All rats exposed to approximately 5,200 ppm died within 8 hr [ACGIH 1991a]. Autopsies of animals chronically exposed at 2,000 to 5,000 ppm for extended (not further specified) periods showed injury to the lungs, brain, liver, and kidneys [AIHA 1978].

2. *Effects on Humans*: n-Amyl acetate is an irritant of the eyes, skin, and mucous membranes in humans; at high concentrations, it causes narcosis. At concentrations above 300 ppm, exposure causes burning of the eyes and conjunctival hyperemia [Grant 1986]. The lowest toxic concentration reported in humans is 200 ppm for 30 min; exposure to this concentration causes eye irritation and headaches [NIOSH 1991; Proctor et al. 1988]. Prolonged or repeated skin contact with n-amyl acetate liquid causes defatting and irritation and may lead to dermatitis [AIHA 1978].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-amyl acetate can cause headache, dizziness, cardiac arrhythmia, narcosis, nausea, pulmonary edema, and irritation of the eyes, nose, and throat. Skin contact with liquid n-amyl acetate results in irritation, and eye contact causes irritation, redness, and a burning sensation.

2. *Chronic exposure*: Chronic exposure to n-amyl acetate can cause defatting of the skin and contact dermatitis.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-amyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-amyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-amyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-amyl acetate and may result in worker exposures to this substance:

—Use of n-amyl acetate as a vehicle solvent in the manufacture of cellulose nitrate lacquers, lacquer thinners, adhesives, paints, enamels, enamel removers, nitrate cements, and film cements

—Spray, hand, brush, or coating applications of paints, lacquers, lacquer thinners, film cements, enamels, adhesives, nitrate cements, and enamel removers

—Extraction of penicillin from fermentation broth during production of antibiotics

—Manufacture of photographic film, quick-drying inks, metallic inks, transfer inks, and artificial fruit-flavoring agents

—Use of n-amyl acetate as a vehicle solvent during molding operations in the manufacture of cellulose nitrate plastics, toys, eyeglass frames, combs, and novelties

—Manufacture of furniture polish, leather polish, and shoe polish

—Pre-spotting and spotting operations in the dry cleaning *industry*

The following methods are effective in controlling worker exposures to n-amyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures.

To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with potential for exposure to n-amyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-amyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-amyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-amyl acetate on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-amyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-amyl acetate is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the n-amyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.08. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If n-amyl acetate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with n-amyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of n-amyl acetate, particularly its potential for causing irritation.

A worker who handles n-amyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-amyl acetate or a solution containing it is handled, processed, or stored.

STORAGE

n-Amyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of n-amyl acetate should be protected from physical damage and should be stored separately from strong oxidizers, strong alkalies, nitrates, strong acids, heat, sparks, and open flame. To prevent static sparks, metal storage containers should be bonded and electrically grounded. All tools and equipment used to open or close containers of n-amyl acetate should be of the nonsparking type. Drums used to store n-amyl acetate must be equipped with self-closing valves, pressure-vacuum bungs, and flame arresters. Because empty containers that formerly contained n-amyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-amyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove any hot metal surface and all sources of heat and ignition.
4. Provide maximum explosionproof ventilation.
5. Use nonsparking tools for cleanup.
6. Absorb liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the n-amyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Amyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of a hazardous substance into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for n-amyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-amyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-amyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act of 1976 as amended (RCRA) [42 U.S.C. 690 et seq], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of n-amyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous substances to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-amyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with n-amyl acetate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyvinyl alcohol has demonstrated good-to-excellent resistance to permeation by n-amyl acetate, withstanding permeation for more than 4 but fewer than 8 hr. Butyl rubber has demonstrated limited resistance to permeation. Natural rubber, neoprene, nitrile rubber, Viton®, and polyvinyl chloride have demonstrated poor resistance to permeation by n-amyl acetate.

If n-amyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-amyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-amyl acetate. Contact lenses should not be worn if the potential exists for n-amyl acetate exposure.

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ACGIH [1991a]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR sec-AMYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about sec-amyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{14}O_2$

- **Structure**

$CH_3COOCH(CH_3)C_3H_7$

- **Synonyms**

2-Pentyl acetate, 2-pentanol acetate, 1-methylbutyl acetate, 2-acetoxypentane

- **Identifiers**

1. CAS No.: 626-38-0
2. RTECS No.: AJ2100000
3. DOT UN: 1104 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

sec-Amyl acetate is a flammable, colorless liquid with a mild, transient, pear- or banana-like odor. The odor threshold is reported to be between 0.002 and 0.08 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.2
2. *Boiling point (at 760 mm Hg):* 121°C (249°F)
3. Specific gravity (water = 1): 0.87 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of sec-amyl acetate): 4.5
5. Melting point: −78°C (−109°F)
6. Vapor pressure at 20°C (68°F): 7 mm Hg
7. Solubility: Slightly soluble in water; soluble in alcohol and ether
8. Evaporation rate (butyl acetate = 1): 0.9

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame
2. Incompatibilities: Fires and explosions may result in contact of sec-amyl acetate with nitrates, strong oxidizers, strong alkalies, or strong acids.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released when sec-amyl acetate is heated to decomposition.
4. Special precautions: sec-Amyl acetate may soften or dissolve plastics.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to sec-amyl acetate.

1. Flash point: 32°C (89°F) (closed cup)
2. *Autoignition temperature: Data not available*

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3. Flammable limits in air (% by volume): Lower, 1.0; upper, 7.5

4. Extinguishant: Use dry chemical, Halon®, alcohol foam, water spray, or carbon dioxide for small fires involving sec-amyl acetate; use water spray, fog, or alcohol foam for large fires involving this substance. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving sec-amyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of sec-amyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving sec-amyl acetate. Firefighters' protective clothing may not provide protection against permeation by sec-amyl acetate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for sec-amyl acetate is 125 ppm (650 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 125 ppm (650 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned sec-amyl acetate a threshold limit value (TLV) of 125 ppm (665 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye and respiratory tract irritation associated with exposure to sec-amyl acetate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to sec-amyl acetate can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: sec-Amyl acetate is an irritant of the eyes, skin, and respiratory tract in animals; at high concentrations, this substance is a narcotic. Guinea pigs exposed to a 2,000 ppm experienced eye and nose irritation; at 5,000 ppm, these animals showed signs of narcosis and congestion of the lungs, with symptoms of incoordination occurring in 90 min and unconsciousness in 5 hr [ACGIH 1991a]. The lowest lethal concentration (LC_{Lo}) in guinea pigs is 10,000 ppm for 5 hr [NIOSH 1991]. At autopsy, acutely poisoned animals showed slight congestion of the brain, lungs, liver, and kidneys [ACGIH 1991a; Clayton and Clayton 1981]. No chronic systemic effects have been reported.

2. *Effects on Humans*: sec-Amyl acetate is an irritant of the eyes, nose, throat, and upper respiratory tract in humans. Humans exposed to 200 ppm for 3 to 5 min experienced mild eye and nose irritation and severe throat irritation [Proctor and Hughes 1978; NIOSH 1991], and exposure to 300 ppm caused bloodshot eyes [Proctor and Hughes 1978; Clayton and Clayton 1981]. An exposure to 1,000 ppm for 1 hr caused serious (not further specified) toxic effects [Proctor et al. 1988]. On the basis of effects seen in animals, exposure to high concentrations of this substance is likely to cause narcosis [Proctor et al. 1988]. Repeated exposure of the skin to liquid sec-amyl acetate causes dermatitis [Proctor and Hughes 1978]. No chronic systemic effects have been reported in humans.

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to sec-amyl acetate can cause eye irritation with pain and redness, and skin irritation and dermatitis.

2. *Chronic exposure*: Prolonged or repeated contact of the skin with sec-amyl acetate can cause defatting of the skin and dermatitis.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of sec-amyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of sec-amyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if sec-amyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve sec-amyl acetate and may result in worker exposures to this substance:

—Application of lacquers, varnishes, enamels, and metallic paints

—Use of sec-amyl acetate as a solvent for chlorinated rubber, nitrocellulose, ethyl cellulose, celluloid products, cements, coated papers, lacquers, and plastic wood

—Manufacture of artificial leather, leather-finish linoleum, photographic film, artificial silk, and furniture polish

—Manufacture of nail enamels, textile printing and sizing compounds, metallic paints, perfumes, pearlescent coatings, printing compounds, and washable wallpaper

The following methods are effective in controlling worker exposures to sec-amyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to sec-amyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may increase risk when a worker is exposed to sec-amyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic eye, skin, or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to sec-amyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of sec-amyl acetate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for sec-amyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne sec-amyl acetate is determined by using a solid sorbent tube containing coconut shell charcoal (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the sec-amyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.12. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If sec-amyl acetate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with sec-amyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of sec-amyl acetate, particularly its potential to be irritating to the skin.

A worker who handles sec-amyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where sec-amyl acetate or a solution containing sec-amyl acetate is handled, processed, or stored.

STORAGE

sec-Amyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of sec-amyl acetate should be protected from physical damage and should be stored separately from oxidizers, nitrates, strong alkalies, strong acids, heat, sparks, and open flame. To prevent static sparks, metal containers used to transfer this substance should be bonded and grounded. Only nonsparking tools should be used when handling containers of sec-amyl acetate. Because empty containers that formerly contained sec-amyl acetate may contain product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving sec-amyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use nonsparking tools for cleanup.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the sec-amyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

sec-Amyl acetate is not subject to EPA's emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulations resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for sec-amyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of sec-amyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although sec-amyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of sec-amyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of sec-amyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with sec-amyl acetate. Solvent-resistant gloves and clothing are recommended. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyvinyl alcohol has been tested against permeation by this substance and has demonstrated good-to-excellent resistance.

If sec-amyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which sec-amyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with sec-amyl acetate. Contact lenses should not be worn if the potential exists for exposure to sec-amyl acetate.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANILINE

INTRODUCTION

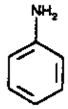
This guideline summarizes pertinent information about aniline for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_5NH_2$

- **Structure**



- **Synonyms**

Aminobenzene, aminophen, aniline oil, benzenamine, blue oil, kyanol, krystallin, cyanol, phenylamine

- **Identifiers**

1. CAS No.: 62-53-3
2. RTECS No.: BW6650000
3. DOT UN: 1547 57
4. DOT label: Poison

- **Appearance and odor**

Aniline is an oily, colorless to brown, combustible liquid that darkens on exposure to air and light. It has the characteristic aromatic amine-like odor. The odor threshold is reported to be 1.1 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 93.12
2. Boiling point (at 760 mm Hg): 184°C (363°F)
3. Specific gravity (water = 1): 1.02 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of aniline): 3.22
5. Melting point: −6.3°C (20.7°F)
6. Vapor pressure at 20°C (68°F): 0.68 mm Hg
7. Solubility: Moderately soluble in water; miscible with alcohol, benzene, chloroform, and most organic solvents
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. The vapors of aniline form explosive mixtures with air.
2. Incompatibilities: Fires and explosions may result from contact with halogens, acids (including nitric and sulfuric acids), oxidizing agents (perchlorates, peroxides, perchromates, etc.), ozone, and trichloromelamine or hexachloromelamine.
3. Hazardous decomposition products: Toxic gases (such as ammonia, carbon oxides, and nitrogen oxides) may be released when aniline is heated and/or decomposes.
4. Special precautions: Liquid aniline attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to aniline.

1. Flash point: 70°C (158°F) (closed cup)
2. Autoignition temperature: 615°C (1,139°F)

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

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3. Flammable limits in air (% by volume): Lower, 1.3; upper, 11

4. Extinguishant: Use carbon dioxide, dry chemical, Halon®, water spray, or standard foam to fight fires involving aniline; never direct a solid stream of water into burning pools of liquid aniline because this will scatter and spread the fire. Water may be used to disperse vapors or to protect persons attempting to stop the leak.

Fires involving aniline should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny entry to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Cylinders of aniline may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of cylinders. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving aniline. Chemical protective clothing that is specifically recommended for aniline may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by aniline.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) PEL for aniline is 2 ppm (8 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that percutaneous absorption is a route of exposure (including mucous membranes and eyes) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has recommended that aniline be designated a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration. Contact with the worker's skin should be minimized [NIOSH 1990, 1992b].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned aniline a threshold limit value (TLV) of 2 ppm (7.6 mg/m^3) as a TWA and has also assigned aniline a "Skin" notation [ACGIH 1991b].

- **Rationale for limits**

OSHA and ACGIH limits are based on the risk of methemoglobinemia associated with exposure to aniline. The NIOSH cancer designation is based on significant evidence of increased bladder cancer in humans [NIOSH 1990].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to aniline can occur through inhalation and by absorption through the eyes or skin.

- **Summary of toxicology**

1. *Effects on Animals*: Aniline causes methemoglobinemia in animals. Head-only versus whole-body exposure of rats for 4 hr resulted in LC$_{50}$s of 839 ppm and 478 ppm, respectively. These data demonstrate the significant extent to which dermal absorption occurs during ambient exposures. The dermal LD$_{50}$ in rabbits is 820 mg/kg [NIOSH 1992a]. The oral LD$_{50}$ in rats is 250 mg/kg, and the lowest lethal concentration in the same species is 250 ppm for 4 hr [NIOSH 1992a]. Dogs, rats, guinea pigs, and mice were exposed to 5 ppm daily for 6 months; no adverse effects were seen in these animals, except that rats developed a moderate degree of methemoglobinemia [Oberst et al. 1956]. At autopsy, rats given aniline for 5, 10, or 20 days showed splenic congestion, increased hematopoiesis, and bone marrow hyperplasia [NLM 1990]. The threshold for methemoglobinemia in rats required an exposure of 90 ppm for 4 hr. In vivo experiments with aniline induced DNA damage in the livers and kidneys of rats, and sister chromatid exchanges in the bone marrow cells of mice [NLM 1990]. In a single oral bioassay in mice and rats, aniline hydrochloride caused a significant increase in the incidence of hemangiosarcomas, sarcomas, and fibrosarcomas of the spleen and of fibrosarcomas and sarcomas of multiple body organs [NCI 1978; IARC 1987]. Based on this evidence, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of aniline in animals is limited [IARC 1987].

2. *Effects on Humans*: Exposure to aniline causes the formation of methemoglobin, which results in a functional anemia that interferes with the ability of the blood to carry oxygen. Aniline is particularly dangerous because of the ease with which this substance is absorbed by the body after inhalation of the vapors or after contact of the skin with either the vapors or liquid. The oral aniline dose estimated to be lethal to 50% of exposed individuals is between 15 and 30 g, although as little as 1 g has caused mortality [Proctor et al.

1988]. Several deaths have been reported in workers acutely poisoned by aniline; cyanosis preceded death from asphyxiation [ACGIH 1991a]. Human volunteers exposed to aniline concentrations in the range of 7 to 53 ppm showed mild signs of cyanosis; increasing the concentration to 100 or 160 ppm for 1 hr caused serious signs and symptoms [Proctor et al. 1988]. Oral administration of 25 to 65 mg to adult volunteers caused a significant dose-dependent elevation in methemoglobin in the blood [Proctor et al. 1988]. Some studies suggest that chronic exposure to low concentrations of aniline is associated with the development of anemia, digestive disturbances, lack of energy, and headache [Proctor et al. 1988]. Early studies of workers exposed to aniline and to other chemicals, including some known bladder carcinogens, showed an excess of bladder cancer deaths. Studies in workers exposed to aniline alone have shown no excess risk of bladder cancer, although these studies are generally methodologically inadequate in various respects. Based on this evidence, IARC has concluded that the epidemiologic evidence of carcinogenicity is inadequate for aniline [IARC 1987]. An epidemiologic study of workers exposed to aniline and o-toluidine showed an increased risk of bladder cancer among exposed workers [NIOSH 1989, 1990]. The effects of o-toluidine and aniline could not be separated epidemiologically.

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to aniline can induce bluish discoloration of the lips, nose, earlobes, and nailbeds; headache; weakness; irritability; drowsiness; dizziness; ringing in the ears; difficult breathing; lethargy; incoordination; rapid heart beat; and unconsciousness. The onset of these signs and symptoms may be delayed as long as 4 hr after exposure. Hemolytic anemia, jaundice, and wine-colored urine may occur after severe overexposure, and these signs may be delayed for as long as 1 week after exposure.

2. *Chronic exposure*: Chronic exposure to aniline may cause headache, anemia, gastrointestinal disturbances, and lethargy. Workers who have been exposed to aniline should be notified that they may be at increased risk of bladder cancer, and they should be alerted to its signs and symptoms. These include (1) blood in the urine, (2) other changes in the appearance of the urine, (3) changes in urinary habits, (4) lumps in the groin or lower abdomen, and (5) pain in the lower abdomen or back [NIOSH 1990].

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Immediately rinse concentrated solutions, vapors, mists, or aerosols of aniline from the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Aniline can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If vapors, mists, or aerosols of aniline are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if aniline or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve aniline and may result in worker exposures to this substance:

—Manufacture of rigid polyurethanes; chemical synthesis of intermediates for dyestuffs and rubber processing; production of methylenediphenyl isocyanate and polymethylene polyphenylisocyanate

—Synthesis of pharmaceuticals, intermediates for pharmaceuticals, hydroquinone for photographic processing, and intermediates for agricultural chemicals

—Manufacture of cloth-marking inks, indelible inks, and lithographic and other printing inks

—Production of monomers for use in nylon fiber manufacture and synthesis of resins

—Manufacture of perfumes, varnishes, black shoe polishes, solvents, paint removers, optical whitening agents, laboratory reagents, and wood stains

The following methods are effective in controlling worker exposures to aniline, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. *Fundamentals of industrial hygiene.* Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to aniline, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the cardiovascular system, blood, liver, and kidneys. A complete blood count also should be performed.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to aniline at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with cardiovascular system, blood, liver, or kidney diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to aniline exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of aniline on the cardiovascular system, blood, liver, and kidneys. A complete blood count should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Since aniline is a potential bladder carcinogen, exposed workers should have an annual urine analysis, including microscopic examination for microhematuria and cytologic examination for neoplastic cells [NIOSH 1990].

Biological monitoring involves sampling and analysis of body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. p-Amino-phenol, a metabolite of aniline, can be measured in the urine of exposed workers. A concentration of 50 mg of total p-aminophenol per liter of urine correlates with an airborne exposure to

2 ppm. The sample should be collected at the end of the exposure period or in the first few hours after the cessation of exposure [ACGIH 1986]. A second method of monitoring for aniline exposure is to measure the methemoglobin concentration of the blood; methemoglobinemia is the first sign of excessive aniline exposure. A methemoglobin level of 1.5% in a specimen taken at the end of the exposure period or shift is a nonspecific indicator of exposure to aniline or other methemoglobinemia-inducing agents [ACGIH 1986].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne aniline is determined by using silica gel tubes (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 30 liters is collected. The sample is then treated with 95% ethanol to extract the aniline. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 2002 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Incidents involving dermal exposure to aniline should be treated as an emergency. Workers should flush the affected areas immediately with plenty of water for 15 min and then thoroughly wash with soap and water. All areas of the body, including the scalp, hair, fingernails, and toenails, should be scrubbed carefully.

Clothing contaminated with aniline should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the contaminated clothing should be informed of the hazardous properties of aniline, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles aniline should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where aniline is handled, processed, or stored.

STORAGE

Aniline should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers should be inspected regularly for leakage. Containers of aniline should be protected from physical damage and should be separated from oxidizers, acids, and other incompatible chemicals, sunlight, heat, sparks, and open flame. Because containers that formerly contained aniline may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving aniline, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate atmosphere to reduce concentration.
5. Protective clothing and respiratory equipment must be worn by cleanup personnel to prevent any skin and eye contact or vapor inhalation; cleanup personnel also should work upwind or use optimum exhaust ventilation.
6. Absorb spilled material with clay, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 1,000 lb or more of aniline onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for aniline is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of aniline per calendar year are required [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of aniline emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Aniline is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U012. Aniline is approved for land disposal as long as its concentration in the waste or treatment residual does not exceed 14 mg/kg. Aniline may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of aniline exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Because aniline can be readily absorbed through the skin, protective clothing should be worn to prevent any possibility of skin contact with liquid aniline or aniline vapors. In work areas where there is a potential for dermal exposure to aniline, gloves, boots, aprons, and gauntlets should be worn. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by aniline and may provide protection for periods greater than 8 hr: butyl rubber and polyvinyl alcohol. Materials that may withstand permeation for more than 4 hr but fewer than 8 hr are Teflon®, Saranex®/Tynek®, and polyethylene/ethylene vinyl alcohol (e.g., 4H® or Silver Shield®). Natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by aniline. Polyethylene has questionable value as a protective material.

If aniline is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which aniline might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with aniline. Contact lenses should not be worn if the potential exists for aniline exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANISIDINE (o-, p-ISOMERS)

INTRODUCTION

This guideline summarizes pertinent information about anisidine (both the ortho- and the para-isomers) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

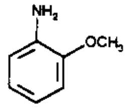
SUBSTANCE IDENTIFICATION

o-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

o-Methoxyaniline, 2-methoxyaniline, 2-aminoanisole, o-anisylamine, 2-methoxybenzenamine, o-methoxyphenylamine

- **Identifiers**

1. CAS No.: 90-04-0
2. RTECS No.: BZ5410000
3. DOT UN: 2431 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

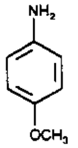
The ortho- form of anisidine is a reddish or yellowish liquid that has a characteristic amine (fishy) odor.

p-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

p-Methoxyaniline, 4-methoxyaniline, 4-methoxybenzenamine, p-anisylamine, p-aminoanisole, 4-aminoanisole

- **Identifiers**

1. CAS No.: 104-94-9
2. RTECS No.: BZ5450000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

The para- form of anisidine is a light reddish-brown, fused crystalline mass that has a characteristic amine (fishy) odor.

CHEMICAL AND PHYSICAL PROPERTIES

o-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2
2. Boiling point (at 760 mm Hg): 225°C (437°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-anisidine): 4.3
5. Melting point: 5°C (41°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Practically insoluble in water; miscible with alcohol and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: o-Anisidine is volatile with steam and unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to o-anisidine.

1. Flash point: 118°C (244°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

p-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2

2. Boiling point (at 760 mm Hg): 246°C (475.4°F)

3. Specific gravity (water = 1): 1.07 at 57°C (134.6°F)

4. Vapor density (air = 1 at boiling point of p-anisidine): 4.3

5. Melting point: 57°C (134.6°F)

6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

7. Solubility: Sparingly soluble in water; freely soluble in methanol, ethanol, and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: p-Anisidine is unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products (both isomers): Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

p-Anisidine is considered a severe fire hazard, but the National Fire Protection Association has not assigned a flammability hazard rating to this chemical.

1. Flash point: 30°C (86°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for anisidine (both isomers) is 0.5 mg/m^3 (0.1 ppm) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as an 8-hr TWA for both the para- and ortho-isomers. The NIOSH REL also bears a "Skin" notation. NIOSH considers the ortho-isomer to be a potential occupational carcinogen; exposure should therefore be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned both isomers of anisidine a threshold limit value (TLV) of 0.5 mg/m^3 (0.1 ppm) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to anisidine [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of systemic effects associated with exposure to anisidine. NIOSH considers o-anisidine to be a potential occupational carcinogen because of positive carcinogenic results in studies of rats and mice.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o- and p-anisidine can occur through inhalation of the dust or vapor, ingestion, or eye or skin contact. Anisidine is readily absorbed through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: Anisidine causes methemoglobinemia and is a carcinogen in experimental animals. The toxicologic literature is often unclear about the particular isomer or mixture of isomers involved in a given study; when information about the specific form of anisidine is available, it is included in the following discussion. The oral LD_{50} in rats is 2,000 mg/kg for o-anisidine and 810 mg/kg for p-anisidine [NIOSH 1991]. Mice exposed to anisidine (isomer not specified) at 2 to 6 ppm for 2 hr/day for 1 year developed anemia and reticulocytosis [Proctor et al. 1988]. Animals that received subacute doses of either of the anisidine isomers developed anemia and other blood changes and showed signs of kidney damage at autopsy [IARC 1982]. Mice and rats fed diets containing up to 30,000 mg/kg o-anisidine hydrochloride for 7 weeks showed reductions in weight gain, and animals fed lower doses for the same period showed blackened, granular, and/or enlarged spleens [IARC 1982]. Eight-week feeding studies involving p-anisidine hydrochloride caused similar effects in rats and mice [IARC 1982]. o-Anisidine hydrochloride in the diet caused transitional-cell carcinomas of the urinary bladder in both rats and mice [IARC 1982]. The rats in this study also had statistically increased numbers of renal transitional-cell carcinomas and thyroid follicular-cell carcinomas [IARC 1982]. p-Anisidine hydrochloride did not cause cancer in mice, and the results of a carcinogenicity bioassay in rats were inconclusive [IARC 1982]. On the basis of this evidence, the International Agency for Research on Cancer (IARC) has concluded that sufficient evidence exists for the carcinogenicity of o-anisidine hydrochloride in animals but not for p-anisidine [IARC 1982].

2. *Effects on Humans*: Anisidine causes methemoglobinemia in humans. Some members of a group of workers exposed to 0.4 ppm of anisidine (isomer not specified) for 6 months (3.5 hr/day) did not exhibit clinical signs of anemia but showed the following blood changes: increased methemoglobin, sulfhemoglobin, and Heinz body formation [Proctor et al. 1988]. Anisidine (form not specified) causes dermatitis on repeated or prolonged contact and is also known to be a mild skin sensitizer [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to anisidine can cause methemoglobinemia, including bluish coloring of the skin, ear lobes, and lips; headache; dizziness; drowsiness; nausea and vomiting; and, in severe cases, unconsciousness and death.

2. *Chronic exposure*: Chronic exposure to anisidine can cause anemia, pallor, methemoglobinemia, fatigue, shortness of breath, and palpitations. Dermatitis and skin sensitization (which include redness and itching of the skin, blisters, swelling, and pain) may also occur. Because three cancer sites (bladder, kidney, and thyroid) have been found in animals, exposure to o-anisidine may cause cancers in humans.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of anisidine. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If the particulates, vapors, mists, or aerosols of anisidine are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to swab particulates from the nostrils

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if anisidine or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve anisidine and may result in worker exposures to this substance:

—Manufacture of azo- or triphenyl-methane dyes and intermediates

—Production of a derivative that is used as an expectorant in drugs for humans and animals and as a muscle relaxant in drugs for humans

—Preparation of organic compounds, synthesis of guaiacol and hair dyes

—Use of anisidine as a corrosion inhibitor for steel storage, as an antioxidant for some polymercaptan resins, and as a dye assist

—Use of anisidine as an analytic agent and as an intermediate in the synthesis of compounds in the form of liquid crystals

—Use of anisidine in the production of pharmaceutical and textile-processing chemicals

The following methods are effective in controlling worker exposures to anisidine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to anisidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be done.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to anisidine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic blood disorders, chronic liver or kidney disease, or chronic cardiovascular disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to anisidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of anisidine on the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of methemoglobin in the blood is a nonspecific, qualitative indicator of exposure to a variety of chemical agents such as anisidine that induce the formation of methemoglobin. Methemoglobin levels cannot be linked quantitatively to airborne concentrations of anisidine; methemoglobin monitoring thus serves only as a screening test to identify workers who may be overexposed. A methemoglobin level of 1.5% of total hemoglobin is recommended by some sources as a biological exposure index. Blood specimens should be collected while exposure to anisidine is occurring, and, if possible, the specimens should be analyzed at the place of collection.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne anisidine (o-, p-isomers) is determined by using XAD-2 solid sorbent tubes (150/75-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 320 liters is collected. The sample is then treated with methanol to extract the anisidine. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet absorption detector. The limit of detection for this procedure is 0.35 µg per sample. This method is described in Method 2514 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Workers should immediately and thoroughly wash with soap and water any areas of the skin that have come in contact with the substance because anisidine can be absorbed through the skin in toxic amounts.

Clothing and shoes contaminated with anisidine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of anisidine, particularily its potential for being absorbed through the skin in toxic amounts.

A worker who handles anisidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where anisidine or a solution containing anisidine is handled, processed, or stored.

STORAGE

Anisidine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas for p-anisidine should be suitable for combustible solids. Containers of anisidine should be protected from physical damage and should be separated from oxidizing agents, heat, sparks, and open flame. Metal conveying and storage equipment should be grounded and bonded to prevent sparks. Bulk storage systems should be of explosionproof design. Because containers that formerly contained anisidine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving anisidine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Make sure that cleanup personnel wear appropriate protective clothing and equipment to prevent skin and eye contact and inhalation.

6. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the anisidine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous release, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Anisidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of anisidine; there is no reportable quantity for anisidine.

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of anisidine emitted or released from their facility.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although anisidine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of anisidine are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of anisidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any skin contact with anisidine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to anisidine permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to anisidine.

If anisidine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which anisidine dust or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with anisidine. Contact lenses should not be worn if the potential exists for anisidine exposure.

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Occupational Health Guideline for Anisidine (o,p-Isomers)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $NH_2C_6H_4OCH_3$
- Synonyms: o-Methoxyaniline; p-methoxyaniline
- Appearance and odor: Ortho: Cololorless to pink liquid with a characteristic amine odor; Para: Light red-brown solid with a characteristic amine odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for anisidine is 0.5 milligram of anisidine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Anisidine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to anisidine may affect the ability of the blood to carry oxygen. The earliest effect may be a bluish color of the skin, especially the lips. If the lack of oxygen becomes severe, a person may have drowsiness, headache, nausea, and vomiting. If oxygen lack is very severe, it may cause unconsciousness and even death.

- **Reporting Signs and Symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to anisidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to anisidine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, kidneys, liver, and cardiovascular system should be stressed.

—A complete blood count: Anisidine has been shown to cause methemoglobinemia and the formation of erythrocytic inclusion bodies. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The absorption of the ortho or para isomer of anisidine, whether from inhalation of the vapor or dust or from skin absorption, causes anoxia due to the formation of methemoblobin. The peroral LD50 in rats was 1.4 g/kg. Mice repeatedly exposed to concentrations of 10 to 30 mg/m^3 for 2 hours daily showed a decrease in the excitability of nerves at the end of 1 month of exposure; after 12 months of exposure there was anemia and reticulocytosis. Workers exposed to a concentration of 1.9 mg/m3 for 3-½ hours per day for 6 months did not develop anemia or specific signs of intoxication; there were some cases of headache and vertigo, which may have been related to the observation of increased methemoglobin and sulfhemoglobin; the presence of erythrocytic inclusions, or Heinz bodies, was observed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 123

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

2. Boiling point (760 mm Hg): Ortho: 225 C (436 F); Para: 243 C (470 F)

3. Specific gravity (water = 1): 1.1 (both isomers)

4. Vapor density (air = 1 at boiling point of anisidine, ortho and para isomers): 4.25

5. Melting point: Ortho: 6.2 C (43 F); Para: 58.5 C (137 F)

6. Vapor pressure at 20 C (68 F): Less than 0.1 mm Hg (both isomers)

7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 1.3; Para: moderate

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released when anisidine decomposes.

4. Special precautions: Liquid anisidine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Para: 30 C (86 F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Anisidine (o,p-isomers) is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for anisidine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with solid or liquid anisidine or liquids containing anisidine, where skin contact may occur.
- If employees' clothing may have become contaminated with solid or liquid anisidine or liquids containing anisidine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with anisidine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of anisidine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the anisidine, the person performing the operation should be informed of anisidine's hazardous properties.
- Where exposure of an employee's body to solid or liquid anisidine or liquids containing anisidine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with anisidine should be removed immediately and not reworn until the anisidine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid anisidine or liquids containing anisidine may contact the eyes.

SANITATION

- Skin that becomes contaminated with anisidine should be immediately washed or showered with soap or mild detergent and water to remove any anisidine.
- Eating and smoking should not be permitted in areas where solid or liquid anisidine or liquids containing anisidine are handled, processed, or stored.
- Employees who handle solid or liquid anisidine or liquids containing anisidine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to anisidine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of azo or triphenylmethane dyes and intermediates; use in preparation of organic compounds; in synthesis of guaicol	General dilution ventilation; personal protective equipment
Use in synthesis of hair dyes; as corrosion inhibitors for steel storage; as an antioxidant for some polymercaptan resins; and as a dyeing assist	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If anisidine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid anisidine or liquids containing anisidine get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solid or liquid anisidine or liquids containing anisidine penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of anisidine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solid or liquid anisidine or liquids containing anisidine have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If anisidine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing anisidine should be absorbed in vermiculite, dry sand, earth, or a similar material. Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal method:

Anisidine may be disposed of in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ANISIDINE (o,p-ISOMERS)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.
5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANISIDINE (o-, p-ISOMERS)

INTRODUCTION

This guideline summarizes pertinent information about anisidine (both the ortho- and the para-isomers) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

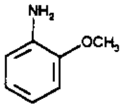
SUBSTANCE IDENTIFICATION

o-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

o-Methoxyaniline, 2-methoxyaniline, 2-aminoanisole, o-anisylamine, 2-methoxybenzenamine, o-methoxyphenylamine

- **Identifiers**

1. CAS No.: 90-04-0
2. RTECS No.: BZ5410000
3. DOT UN: 2431 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

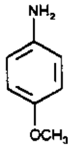
The ortho- form of anisidine is a reddish or yellowish liquid that has a characteristic amine (fishy) odor.

p-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

p-Methoxyaniline, 4-methoxyaniline, 4-methoxybenzenamine, p-anisylamine, p-aminoanisole, 4-aminoanisole

- **Identifiers**

1. CAS No.: 104-94-9
2. RTECS No.: BZ5450000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

The para- form of anisidine is a light reddish-brown, fused crystalline mass that has a characteristic amine (fishy) odor.

CHEMICAL AND PHYSICAL PROPERTIES

o-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2
2. Boiling point (at 760 mm Hg): 225°C (437°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-anisidine): 4.3
5. Melting point: 5°C (41°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

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Division of Standards Development and Technology Transfer

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7. Solubility: Practically insoluble in water; miscible with alcohol and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: o-Anisidine is volatile with steam and unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to o-anisidine.

1. Flash point: 118°C (244°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

p-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2

2. Boiling point (at 760 mm Hg): 246°C (475.4°F)

3. Specific gravity (water = 1): 1.07 at 57°C (134.6°F)

4. Vapor density (air = 1 at boiling point of p-anisidine): 4.3

5. Melting point: 57°C (134.6°F)

6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

7. Solubility: Sparingly soluble in water; freely soluble in methanol, ethanol, and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: p-Anisidine is unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products (both isomers): Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

p-Anisidine is considered a severe fire hazard, but the National Fire Protection Association has not assigned a flammability hazard rating to this chemical.

1. Flash point: 30°C (86°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for anisidine (both isomers) is 0.5 mg/m^3 (0.1 ppm) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as an 8-hr TWA for both the para- and ortho-isomers. The NIOSH REL also bears a "Skin" notation. NIOSH considers the ortho-isomer to be a potential occupational carcinogen; exposure should therefore be limited to the lowest feasible concentration [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned both isomers of anisidine a threshold limit value (TLV) of 0.5 mg/m^3 (0.1 ppm) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to anisidine [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of systemic effects associated with exposure to anisidine. NIOSH considers o-anisidine to be a potential occupational carcinogen because of positive carcinogenic results in studies of rats and mice.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to o- and p-anisidine can occur through inhalation of the dust or vapor, ingestion, or eye or skin contact. Anisidine is readily absorbed through the skin.

• Summary of toxicology

1. *Effects on Animals*: Anisidine causes methemoglobinemia and is a carcinogen in experimental animals. The toxicologic literature is often unclear about the particular isomer or mixture of isomers involved in a given study; when information about the specific form of anisidine is available, it is included in the following discussion. The oral LD_{50} in rats is 2,000 mg/kg for o-anisidine and 810 mg/kg for p-anisidine [NIOSH 1991]. Mice exposed to anisidine (isomer not specified) at 2 to 6 ppm for 2 hr/day for 1 year developed anemia and reticulocytosis [Proctor et al. 1988]. Animals that received subacute doses of either of the anisidine isomers developed anemia and other blood changes and showed signs of kidney damage at autopsy [IARC 1982]. Mice and rats fed diets containing up to 30,000 mg/kg o-anisidine hydrochloride for 7 weeks showed reductions in weight gain, and animals fed lower doses for the same period showed blackened, granular, and/or enlarged spleens [IARC 1982]. Eight-week feeding studies involving p-anisidine hydrochloride caused similar effects in rats and mice [IARC 1982]. o-Anisidine hydrochloride in the diet caused transitional-cell carcinomas of the urinary bladder in both rats and mice [IARC 1982]. The rats in this study also had statistically increased numbers of renal transitional-cell carcinomas and thyroid follicular-cell carcinomas [IARC 1982]. p-Anisidine hydrochloride did not cause cancer in mice, and the results of a carcinogenicity bioassay in rats were inconclusive [IARC 1982]. On the basis of this evidence, the International Agency for Research on Cancer (IARC) has concluded that sufficient evidence exists for the carcinogenicity of o-anisidine hydrochloride in animals but not for p-anisidine [IARC 1982].

2. *Effects on Humans*: Anisidine causes methemoglobinemia in humans. Some members of a group of workers exposed to 0.4 ppm of anisidine (isomer not specified) for 6 months (3.5 hr/day) did not exhibit clinical signs of anemia but showed the following blood changes: increased methemoglobin, sulfhemoglobin, and Heinz body formation [Proctor et al. 1988]. Anisidine (form not specified) causes dermatitis on repeated or prolonged contact and is also known to be a mild skin sensitizer [Proctor et al. 1988].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to anisidine can cause methemoglobinemia, including bluish coloring of the skin, ear lobes, and lips; headache; dizziness; drowsiness; nausea and vomiting; and, in severe cases, unconsciousness and death.

2. *Chronic exposure*: Chronic exposure to anisidine can cause anemia, pallor, methemoglobinemia, fatigue, shortness of breath, and palpitations. Dermatitis and skin sensitization (which include redness and itching of the skin, blisters, swelling, and pain) may also occur. Because three cancer sites (bladder, kidney, and thyroid) have been found in animals, exposure to o-anisidine may cause cancers in humans.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of anisidine. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If the particulates, vapors, mists, or aerosols of anisidine are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to swab particulates from the nostrils

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if anisidine or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve anisidine and may result in worker exposures to this substance:

—Manufacture of azo- or triphenyl-methane dyes and intermediates

—Production of a derivative that is used as an expectorant in drugs for humans and animals and as a muscle relaxant in drugs for humans

—Preparation of organic compounds, synthesis of guaiacol and hair dyes

—Use of anisidine as a corrosion inhibitor for steel storage, as an antioxidant for some polymercaptan resins, and as a dye assist

—Use of anisidine as an analytic agent and as an intermediate in the synthesis of compounds in the form of liquid crystals

—Use of anisidine in the production of pharmaceutical and textile-processing chemicals

The following methods are effective in controlling worker exposures to anisidine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to anisidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be done.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to anisidine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic blood disorders, chronic liver or kidney disease, or chronic cardiovascular disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to anisidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of anisidine on the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of methemoglobin in the blood is a nonspecific, qualitative indicator of exposure to a variety of chemical agents such as anisidine that induce the formation of methemoglobin. Methemoglobin levels cannot be linked quantitatively to airborne concentrations of anisidine; methemoglobin monitoring thus serves only as a screening test to identify workers who may be overexposed. A methemoglobin level of 1.5% of total hemoglobin is recommended by some sources as a biological exposure index. Blood specimens should be collected while exposure to anisidine is occurring, and, if possible, the specimens should be analyzed at the place of collection.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne anisidine (o-, p-isomers) is determined by using XAD-2 solid sorbent tubes (150/75-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 320 liters is collected. The sample is then treated with methanol to extract the anisidine. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet absorption detector. The limit of detection for this procedure is 0.35 µg per sample. This method is described in Method 2514 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Workers should immediately and thoroughly wash with soap and water any areas of the skin that have come in contact with the substance because anisidine can be absorbed through the skin in toxic amounts.

Clothing and shoes contaminated with anisidine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of anisidine, particularily its potential for being absorbed through the skin in toxic amounts.

A worker who handles anisidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where anisidine or a solution containing anisidine is handled, processed, or stored.

STORAGE

Anisidine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas for p-anisidine should be suitable for combustible solids. Containers of anisidine should be protected from physical damage and should be separated from oxidizing agents, heat, sparks, and open flame. Metal conveying and storage equipment should be grounded and bonded to prevent sparks. Bulk storage systems should be of explosionproof design. Because containers that formerly contained anisidine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving anisidine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Make sure that cleanup personnel wear appropriate protective clothing and equipment to prevent skin and eye contact and inhalation.
6. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the anisidine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous release, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Anisidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of anisidine; there is no reportable quantity for anisidine.

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of anisidine emitted or released from their facility.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although anisidine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of anisidine are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of anisidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any skin contact with anisidine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to anisidine permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to anisidine.

If anisidine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which anisidine dust or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with anisidine. Contact lenses should not be worn if the potential exists for anisidine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANTIMONY AND ITS COMPOUNDS (as Sb)

INTRODUCTION

"Antimony" is defined as elemental antimony and all antimony compounds with the exception of the gas stibine. This guideline summarizes pertinent information about antimony and its compounds for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** Sb
- **Synonyms:** Antimony regulus, stibium
- **Identifiers:** CAS 7440-36-0; RTECS CC402500; DOT 2871, label required: "St. Andrew's Cross (X)"
- **Appearance:** Silvery, white solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data for elemental antimony**

1. Molecular weight: 121.75
2. Boiling point (at 760 mmHg): 1,635°C (2,975°F)
3. Specific gravity (water = 1): 6.68
4. Melting point: 630.5°C (1,116.9°F)
5. Insoluble in water

- **Reactivity**

Incompatibilities: Oxidizing materials and acids, especially halogenated acids, can react with antimony and alloys containing antimony to produce stibine gas (antimony hydride), which is more toxic than the antimony metal alone.

- **Flammability**

1. Extinguishant: Dry graphite, sodium chloride, or potassium chloride
2. Antimony is combustible in powder form or by chemical reaction with nitrates or halogenated compounds.

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on the odor threshold and eye irritation levels, antimony should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for antimony and its compounds (as Sb) is 0.5 milligrams per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for antimony and its compounds (as Sb) is 0.5 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek for antimony and its compounds (as Sb) including antimony trioxide during handling and use. The ACGIH has given antimony trioxide production an A2 designation (an A2 substance is a suspected human carcinogen) without having sufficient evidence to assign a TLV (Table 1).

Table 1.—Occupational exposure limits for antimony and its compounds

	Antimony and compounds (as Sb), mg/m^3	Antimony trioxide production, mg/m^3
OSHA PEL TWA	0.5	—
NIOSH REL TWA	0.5	—
ACGIH TLV® TWA	0.5	(A2)*

* (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Antimony may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• Summary of toxicology

1. *Effects on animals:* Intraperitoneal injection of antimony or its compounds into rats produced an increase in blood eosinophil count, acute congestion of the heart, liver, and kidneys, and death (due to heart failure). Subchronic inhalation of antimony trisulfide by rats and rabbits caused degeneration of the heart muscle and changes in electrocardiograms; subcutaneous injections in rats caused fatty degeneration of the liver and swelling of kidney tubules. Chronic inhalation of antimony trioxide by guinea pigs, rats, or rabbits produced extensive lung inflammation, decreased white blood cell and eosinophil counts, enlargement of splenic follicles, and fatty degeneration of the liver.
2. *Effects on humans:* Exposure of workers to antimony trichloride, antimony trisulfide, or antimony trioxide has caused fibrosis of the lungs (pneumoconiosis), electrocardiogram changes, heart muscle changes, and death due to heart disease. Increased rates of spontaneous late abortions, premature births, and gynecologic problems have been reported for female metallurgic workers exposed to antimony trioxide, antimony pentasulfide, or metallic dust.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to antimony and its compounds can cause gastrointestinal pain, cough, loss of appetite, itching, skin eruptions, and irritation of the skin, eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to antimony and its compounds can cause headache, sleeplessness, dizziness, metallic taste, ulcers, weight loss, nausea, vomiting, diarrhea, impairment of sense of smell, and pain or tightness in the chest.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include the education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include the systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to antimony, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and cardiovascular, reproductive, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to antimony at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical or other findings suggestive of cardiovascular or chronic skin disease. The physician should obtain baseline values for electrocardiographic studies appropriate for the age and medical history of the worker.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to antimony. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and cardiovascular, reproductive, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to antimony may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to antimony should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis of antimony may be performed by collecting with a cellulose membrane filter, digesting with nitric, sulfuric, and perchloric acids, and analyzing by atomic absorption spectrophotometry. Detailed sampling and analytical methods for antimony may be found in the *NIOSH Manual of Analytical Methods* (method numbers 189 and 261).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with antimony.

Workers should be provided with and required to use dust- and splash-proof safety goggles where antimony may come in contact with the eyes.

SANITATION

Clothing which is contaminated with antimony should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of antimony from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of antimony's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with antimony should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle antimony should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to antimony may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for antimony

Operations	Controls
During crushing and transferring antimony ore	Process enclosure, dilution ventilation, and dust control with water
During production of lead/antimony alloys	Local exhaust ventilation
During machining, grinding, buffing, and polishing of metal products containing antimony	Local exhaust ventilation, personal protective clothing
During the manufacture of paints, pigments, enamels, glazes, ceramics, and glass	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to antimony, an eye-wash fountain should be provided within the immediate work area for emergency use.

If antimony gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to antimony, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If antimony gets on the skin, wash it immediately with soap and water. If antimony penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If antimony is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing antimony, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing antimony may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. If in solid form, antimony may be collected and placed in an appropriate container.
5. Antimony may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal of antimony and its compounds are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for antimony and its compounds

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5.0 mg/m^3	Any dust and mist respirator except single-use and quarter-mask respirators, if not present as fume
	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 12.5 mg/m^3	Any powered air-purifying respirator with dust and mist filter, if not present as fume
	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 25 mg/m^3	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 80 mg/m^3	Any supplied-air respirator with a full half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 80 mg/m^3	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 mg/m^3 (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANTU

INTRODUCTION

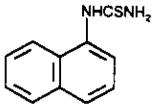
This guideline summarizes pertinent information about ANTU for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{11}H_{10}N_2S$

- **Structure**



- **Synonyms**

α-Naphthylthiourea, 1-naphthalenylthiourea, 1-(1-naphthyl)-2-thiourea, 1-naphthylthiourea, α-naphthylthiocarbamide, Alrato, Anturat, Bantu, Dirax, Kill Kantz, Krysid, Naphtox, Rattrack, Rat-tu, Smeesana

- **Identifiers**

1. CAS No.: 86-88-4
2. RTECS No.: YT9275000
3. DOT UN: 1651 53
4. DOT label: Poison

- **Appearance and odor**

ANTU is a colorless, white, or gray crystalline compound that is odorless. Commercial ANTU preparations are often contaminated with as much as 2% 2-naphthylamine, a recognized human carcinogen. ANTU is no longer manufactured in the United States.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 202.3
2. Boiling point (at 760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of ANTU): 6.99
5. Melting point: 198°C (388.4°F)
6. Vapor pressure at 20°C (68°F): Nearly zero
7. Solubility: Practically insoluble in water, fairly soluble in hot alcohol, and soluble in acetone and triethylene glycol
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires and explosions may result from contact of ANTU with strong oxidizers; ANTU also reacts with silver nitrate.
3. Hazardous decomposition products: Toxic gases (such as sulfur dioxide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving ANTU.
4. Special precautions: None

- **Flammability**

ANTU may burn, but it will not ignite readily.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving ANTU; use water spray, fog, or standard foam to fight large fires involving ANTU.

Fires involving ANTU should be fought upwind and from the maximum distance possible. Isolate the hazard area and

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Division of Standards Development and Technology Transfer

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deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ANTU. Firefighters' protective clothing may not provide protection against permeation by ANTU.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ANTU is 0.3 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for ANTU of 0.3 mg/m^3 as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ANTU a threshold limit value (TLV) of 0.3 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of pulmonary effects associated with exposure to ANTU.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ANTU can occur through inhalation, ingestion, and eye or skin contact; by analogy with other thiourea products, percutaneous absorption of ANTU is likely.

- **Summary of toxicology**

1. *Effects on Animals*: ANTU causes pulmonary edema and pleural effusion in exposed animals. The toxicity of ANTU varies widely among different species of animals but is especially high in adult Norway rats [Hayes 1982]. The oral LD_{50} is 6 mg/kg in rats and 4,250 mg/kg in monkeys [NIOSH 1991]. Sixty percent of rats fed a 35-mg/kg dose of ANTU died; their autopsies revealed interstitial pulmonary edema and pericardial effusions as well as mild liver damage [Proctor et al. 1988]. Rats given lethal doses of ANTU also showed increases in blood sugar, decreases in liver glycogen stores, decreased or absent urine output, and lesions of the kidney at autopsy [Gosselin et al. 1984]. After repeated doses, animals developed a tolerance to the acute toxicity of ANTU [Proctor et al. 1988]. ANTU may have antithyroid properties when administered to animals in sublethal, chronic doses [Gosselin et al. 1984]. ANTU is mutagenic in several in vitro assay systems [Hayes 1982; NIOSH 1991]. Carcinogenicity bioassays in two strains of mice were negative [Hayes 1982].

2. *Effects on Humans*: ANTU is believed to have caused bladder cancer in workers exposed during the application of ANTU-containing rodenticides; however, the causative agent in these cancers may have been β-naphthylamine, which was present in ANTU as an impurity [Orjelick 1975]. A total of 14 cases of urothelial tumors were reported [Davies et al. 1982]. When ingested, ANTU is probably not toxic to humans except in relatively large amounts; on the basis of the results of acute toxicity testing in monkeys, the mean lethal oral dose in humans is estimated to be 4 g/kg [Gosselin et al. 1984]. No reported cases have involved the ingestion of pure ANTU, but accidental or suicidal ingestions of ANTU in combination with other rat poisons have been reported. One man ingested 80 g of a rat poison that contained 30% ANTU and then drank a large amount of alcohol; he subsequently showed the following ANTU-related effects: vomiting, difficult breathing, cyanosis, and fluid in the lungs [Gosselin et al. 1984]. ANTU is reported to have caused contact eczema in one occupationally exposed worker [Hayes 1982]. Workers handling products containing thiourea (such as ANTU) have shown dermal absorption and destructive changes of the thyroid gland [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute inhalation exposure may produce coughing, lung edema, dyspnea, trenchitis, or pneumonitis [NLM 1991]. Ingestion of ANTU can induce vomiting, difficult breathing, blueness of the skin and mucous membranes, and lung edema. Tissue contact can cause eye or skin irritation.

2. *Chronic exposure*: ANTU can cause blood or pus in the urine, pain on urination, and other signs and symptoms of bladder cancer. Hypothyroidism with weight gain, dryness of the skin, eczema, and bradycardia have also been associated with occupational exposure to ANTU.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: ANTU can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of ANTU are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if ANTU or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations involve ANTU and may result in worker exposures to this substance:

—Manufacture of ANTU

—Formulation and use of ANTU as a rodenticide to control the Norway rat

The following methods are effective in controlling worker exposures to ANTU, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ANTU, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the thyroid and adrenal glands, respiratory tract, liver, and bladder. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ANTU at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic respiratory disease, hypothyroidism, other endocrine disease, chronic liver disease, or bladder disorders.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ANTU exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ANTU on the lungs, thyroid, adrenal gland, liver, and bladder. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ANTU.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because exposure to ANTU may cause diseases with long latencies, medical surveillance may need to be continued long after job termination.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ANTU is determined by using a 37-mm, 1-micron polytetrafluoroethylene filter. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 480 liters is collected. The samples are desorbed with methanol. Analysis is conducted by high-performance liquid chromatography using an ultraviolet light detector. The limit of detection for this procedure is 5 µg per sample. This method is described in Method No. S276 of the *NIOSH Manual of Analytical Methods* [NIOSH 1978].

PERSONAL HYGIENE

Because ANTU can be absorbed through the skin in toxic amounts, workers should dust off any solid ANTU from their skin, flush the affected areas immediately with plenty of water for 15 min, and then wash the area twice with soap and water.

Clothing and shoes contaminated with ANTU should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of ANTU, particularly its potential to be hazardous to the respiratory system, bladder, and endocrine system.

A worker who handles ANTU should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ANTU or a solution containing ANTU is handled, processed, or stored.

STORAGE

ANTU should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of ANTU should be protected from physical damage and should be separated from strong oxidizers, heat, sparks, and open flame. Because empty containers may contain ANTU residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ANTU, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete.

The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the atmosphere to reduce the concentration of ANTU.

4. For small dry spills, use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the ANTU for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether these requirements have been changed.

- **Emergency planning requirements**

If 10,000 lb or more of ANTU is present, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30]. If ANTU is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 5,000 lb or more is present at the facility.

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ANTU is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ANTU emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. ANTU is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P072. This substance has been banned from land disposal and may be treated by incineration. ANTU may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ANTU exceeds prescribed exposure limits. Respirators may be used

(1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with ANTU. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to ANTU permeation; however, one source recommends polyethylene to protect against permeation by ANTU. Since specific test data are not available for ANTU, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to ANTU.

If ANTU is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ANTU might contact the eyes (e.g., through dust particles or splashes of ANTU-containing solutions). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ANTU. Contact lenses should not be worn if the potential exists for ANTU exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR INORGANIC ARSENIC AND ITS COMPOUNDS (as As)

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

"Inorganic arsenic" is defined as elemental arsenic and all of its inorganic compounds except arsine (see guideline for arsine). This guideline summarizes pertinent information about inorganic arsenic for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for elemental arsenic.

- **Formula:** As
- **Synonyms:** Arsenic black, arsenic-75, arsenic solid, arsenic metallic, arsenicals, grey arsenic
- **Identifiers:** CAS 7440-38-2; RTECS CG0525000; DOT 1558, label required: "Poison"
- **Appearance and odor:** Gray metal with an odor like garlic when heated

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for elemental arsenic.

- **Physical data**

1. Molecular weight: 74.92
2. Boiling point (at 760 mmHg): 613°C (1,135°F), sublimes
3. Specific gravity (water = 1): 5.73
4. Vapor density (air = 1 at sublimation point of arsenic): 2.6
5. Melting point: Sublimes at 613°C (1,135°F)
6. Insoluble in water

- **Reactivity**

1. Incompatibilities: Oxidizing agents and heat
2. Hazardous decomposition products: Toxic gases and vapors or fumes (e.g., arsenic oxide fume) may be released in a fire involving arsenic.
3. Caution: Hydrogen gas can react with inorganic arsenic to form arsine.

- **Flammability**

1. Extinguishant: All firefighting agents, except soda-acid
2. Caution: Arsenic is combustible in powder form or by chemical reaction with powerful oxidizers such as bromates, chlorates, iodates, and peroxides.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for inorganic arsenic (except arsine) is 0.01 milligrams of arsenic per cubic meter of air (mg/m^3) as a time-weighted average (TWA) over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that arsenic and all its inorganic compounds be controlled and handled as potential human carcinogens in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) for arsenic and all its inorganic compounds is 0.002 mg/m^3 as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for soluble arsenic compounds is 0.2 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH has designated arsenic trioxide production as A2 (suspected human carcinogen) without having sufficient evidence to assign a TLV® (Table 1).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Inorganic arsenic compounds may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for inorganic arsenic and its compounds (as As)

	Arsenic and its inorganic compounds mg/m^3	Arsenic compounds, soluble mg/m^3	Arsenic trioxide production mg/m^3
OSHA PEL TWA	0.01	—	—
NIOSH REL (Ca)*			
Ceiling (15 min)	0.002	—	—
ACGIH TLV® (TWA)	—	0.2	(A2)†

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

- **Summary of toxicology**

1. *Effects on animals:* Chronic ingestion or inhalation of inorganic arsenic by rats caused marked enlargement of the common bile duct and fatty degeneration of the liver. Injection of arsenic in pregnant rats, mice, and hamsters caused malformations of the offspring.
2. *Effects on humans:* Inhalation, ingestion, or dermal exposure of workers to inorganic arsenic has caused peripheral nerve inflammation (neuritis) and degeneration (neuropathy), reduced peripheral circulation, anemia, increased mortality due to cardiovascular failure, and cancers of the skin, lungs, and lymphatic system.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to inorganic arsenic can cause nausea, vomiting, diarrhea, weakness, loss of appetite, cough, chest pain, giddiness, headache, and breathing difficulty (dyspnea).
2. *Long-term (chronic):* Exposure to inorganic arsenic can cause weakness, nausea, vomiting, diarrhea, skin and eye irritation, hyperpigmentation, thickening of the palms and soles (hyperkeratosis), contact dermatitis, skin sensitization, warts, ulceration and perforation of the nasal septum, and numbness and weakness in the legs and feet.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevent environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to inorganic arsenic, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, peripheral nervous system, liver, lymphatic and hematopoietic (blood cell forming) systems, and respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to inorganic arsenic and its compounds at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or peripheral neuropathy, a history and other findings consistent with chronic disease of the skin or nervous system, and significant breathing impairment due to preexisting chronic lung disease.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to inorganic arsenic. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, blood, lymphatic system, peripheral nervous system, liver, and respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to inorganic arsenic and its compounds may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include: Inflammatory and toxic neuropathy, agranulocytosis or neutropenia (absense or a severe decrease in the number of certain white blood cells), and cancers of the liver and respiratory tract.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of inorganic arsenic. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting particulate inorganic arsenic with cellulose membrane filters followed by digestion with acid and analysis by atomic absorption with flame arsine generation. A detailed sampling and analytical method may be found in the *NIOSH Manual of Analytical Methods* (method number 7900).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with inorganic arsenic.

SANITATION

Clothing which is contaminated with inorganic arsenic should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of inorganic arsenic from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of inorganic arsenic's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with inorganic arsenic should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle inorganic arsenic should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to inorganic arsenic may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to inorganic arsenic, an eyewash fountain should be provided within the immediate work area for emergency use.

If inorganic arsenic gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to inorganic arsenic, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If inorganic arsenic gets on the skin, wash it immediately with soap and water. If inorganic arsenic penetrates the clothing, remove the clothing promptly and wash the skin with soap and water. Get medical attention promptly.

Table 2.—Operations and methods of control for inorganic arsenic

Operations	Controls
During the manufacture of insecticides, weed killers and fungicides; during use as a wood preservative	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the manufacture and handling of calcium arsenate; during use in the manufacture of electrical semiconductors, diodes, and solar batteries	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a bronzing or decolorizing addition in glass manufacturing; during use in the production of opal glass and enamels	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an addition to alloys to increase hardening and heat resistance	Process enclosure, local exhaust ventilation, personal protective equipment
During smelting of ores	Local exhaust ventilation, personal protective equipment

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If inorganic arsenic or its compounds are spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities of liquids containing inorganic arsenic, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing inorganic arsenic may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Inorganic arsenic dust may be collected by vacuuming with an appropriate high-efficiency fitration system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for inorganic arsenic

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted acid gas canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ARSINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about arsine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. For information on other arsenic compounds, see guideline for inorganic arsenic.

SUBSTANCE IDENTIFICATION

- **Formula:** AsH_3
- **Synonyms:** Arsenic hydride, arsenic trihydride, hydrogen arsenide
- **Identifiers:** CAS 7784-42-1; RTECS CG6475000; DOT 2188, label required: "Poison, Flammable Gas"
- **Appearance and odor:** Colorless gas with a faint odor like garlic

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 77.95
2. Boiling point (at 760 mmHg): -62.5°C (-80.5°F)
3. Vapor density (air = 1 at boiling point of arsine): 2.69
4. Melting point: -116°C (-177°F)
5. Vapor pressure at 20°C (68°F): >1 atm
6. Solubility in water, g/100 g water at 20°C (68°F): 0.07
7. Ionization potential: 10.03 eV

- **Reactivity**

1. Incompatibilities: Arsine reacts with strong oxidizers, especially chlorine and nitric acid. Arsine decomposes at temperatures above 300°C (572°F) to form elemental arsenic and hydrogen. In the presence of moisture, decomposition may be triggered by light.
2. Hazardous decomposition products: Toxic fumes may be released in a fire involving arsine.

- **Flammability**

Flammable gas

- **Warning properties**

1. Odor threshold: 0.5 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for arsine is 0.05 parts of arsine per million parts of air (ppm) [0.2 milligrams of arsine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that arsenic and all its inorganic compounds including arsine be regarded as potential human carcinogens in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) for arsine is 0.002 mg/m^3 (as arsenic) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.05 ppm (0.2 mg/m^3) for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for arsine

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	0.05	0.2
NIOSH REL (as arsenic) ceiling (15 min) (Ca)*	—	0.002
ACGIH TLV® TWA	0.05	0.2

* (Ca): NIOSH recommends treating as a potential human carcinogen.

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HEALTH HAZARD INFORMATION

- **Routes of exposure**

Arsine may cause adverse health effects following exposure via inhalation.

- **Summary of toxicology**

Effects on humans: Acute inhalation of arsine has caused the breakdown of red blood cells and hemoglobin, impairment of kidney function, damage to the liver and heart, electroencephalogram abnormality (elevation of T-waves), hemolytic anemia, and death due to kidney or heart failure. The human carcinogenic potential of arsine itself has not been determined; however, inorganic arsenic, a recognized human carcinogen in the workplace, is used in the production of arsine.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to arsine can cause the delayed onset of headache, malaise, weakness, dizziness, breathing difficulty (dyspnea), abdominal pain, nausea, vomiting, jaundice, bloody urine followed by absence of urination, pulmonary edema, and coma.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to arsine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiological and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and and integrity of the skin, liver, kidneys, and lymphatic and hematopoietic (blood cell forming), respiratory, and peripheral nervous systems. A complete blood count with a reticulocyte count should be performed. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to arsine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or peripheral neuropathy, a history and other findings consistent with chronic disease of the skin or nervous system, and significant breathing impairment due to preexisting chronic lung disease.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to arsine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, kidneys, and hematopoietic, lymphatic, respiratory, and peripheral nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to arsine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Non-autoimmune hemolytic anemia and acute renal (kidney) failure
2. Delayed-onset SHE's include: Chronic renal (kidney) failure (see also SHE's for inorganic arsenic and its compounds)

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of arsine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by workers) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting arsine using charcoal tubes with prefilters to capture particulates followed by desorption with nitric acid and analysis by atomic absorption spectrophotometry with heated graphite atomization. Direct-reading devices calibrated to measure arsine may also be used if available. A detailed sampling and analytical method for arsine may be found in the *NIOSH Manual of Analytical Methods* (method number 6001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate clothing necessary to prevent skin contact with arsine.

SANITATION

Clothing which is contaminated with arsine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of arsine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of arsine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle arsine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

Contact lenses should not be worn when there is a potential for exposure to arsine.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to arsine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for arsine

Operations	Controls
During the manufacture of electrical semiconductors and gallium arsenide; during the manufacture, storage, and distribution of arsine	Process enclosure, local exhaust ventilation, personal protective equipment
During the refining of of metal ores that may contain arsenic	Local exhaust ventilation, personal protective equipment
During cleaning of metal equipment, electroplating of metals, metallic pickling, soldering and etching, photo-duplication, and use of photographic emulsions	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

If arsine is leaked, the following steps should be taken:

1. Stop the flow of arsine gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Ventilate area of leak.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are done in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning.

The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for arsine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted canister providing protection against the compound of concern Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
ASBESTOS
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about asbestos for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for various forms of asbestos: (1) Asbestos (mixed forms);
(2) Chrysotile;
(3) Amosite;
(4) Crocidolite;
(5) Tremolite;
(6) Anthophyllite;
(7) Actinolite.
If unspecified, data apply to all forms.

- **Composition:** (1) Not Available;
(2) $3MgO-2SiO_2-2H2O$;
(3) $(FeMg)SiO_3$;
(4) $NaFe(SiO_3)_2-FeSiO_3-H_2O$;
(5) $Ca_2Mg_5Si_8O_{22}(OH)_2$;
(6) $(MgFe)_7Si_8O_{22}(OH)_2$;
(7) $CaO-3(MgFe)O-4SiO_2$
- **Synonyms:** (1) Asbestos fiber, serpentine, amphibole;
(2) Canadian chrysotile, white asbestos, serpentine;
(3) Brown asbestos, fibrous grunerite;
(4) Blue asbestos;
(5) Fibrous tremolite;
(6) Azbolen asbestos;
(7) Not available
- **Identifiers:** (1) CAS 1332-21-4; RTECS CI6475000; DOT 2212 (blue) 2590 (white);
(2) CAS 12001-29-5; RTECS CI6478500; DOT 2590;
(3) CAS 12172-73-5; RTECS CI6477000; DOT Not assigned;
(4) CAS 12001-28-4, RTECS CI6479000; DOT 2212;
(5) CAS 14567-73-8; RTECS CI6560000; DOT Not assigned;
(6) CAS 17068-78-9; RTECS CI6478000; DOT Not assigned;
(7) CAS 13768-00-8; RTECS CI6476000; DOT Not assigned
- **Appearance and odor:** A fiber or filament, asbestos may have a "fluffy" appearance. Colors may vary from white, gray, blue, brown, green or yellow. Positive identification requires microscopic examination.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: (2) 277.13; (5) 185.03
2. Specific gravity (water = 1): 2.5-3.0
3. Noncombustible solid

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

Only asbestos fibers greater than 5 micrometers (μ)m in length are considered for the following exposure limits. The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for asbestos is 0.2 fiber per cubic centimeter (cc) of air as a time-weighted average (TWA) concentration over an 8-hour workshift with an action level of 0.1 fiber/cc as an hour TWA. The National Institute for Occupational Safety and Health (NIOSH) recommends that asbestos be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 fiber/cc (in 40-liter air sample) as a TWA concentration for up to an 8-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated asbestos as an A1 substance (suspected human carcinogen, with an assigned threshold limit value/ TLV®) of 2 fibers/cc for chrysotile, 0.5 fiber/cc for amosite, 0.2 fiber/cc for crocidolite, and 2 fibers/cc for other forms, as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Table 1.—Occupational exposure limits for asbestos

	Exposure limits mg/m^3*
OSHA PEL TWA	0.2
Action level	0.1
NIOSH REL TWA (Ca)†	0.1
ACGIH TLV® TWA (A1a)§	
Chrysotile	2.0
Amosite	0.5
Crocidolite	0.2
Other forms	2.0

* Fibers greater than 5 μm in length.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A1a): Human carcinogen with an assigned TLV®.

HEALTH HAZARD INFORMATION

• Routes of exposure

Asbestos may cause adverse health effects following exposure via inhalation or ingestion.

• Summary of toxicology

1. *Effects on animals:* Single intrapleural injections of asbestos in rats, rabbits, and hamsters produced mesothelioma (cancer of the chest or abdominal linings). In rats, chronic inhalation or oral administration of asbestos produced cancers of the lungs, stomach, kidneys, liver, or mammary glands. All forms of asbestos were found to be carcinogenic in treated animals.
2. *Effects on humans:* Exposure to asbestos has been found to significantly increase the risks of contracting asbestosis, lung cancer, and mesothelioma.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to asbestos can cause shortness of breath, chest or abdominal pain, and irritation of the skin and mucous membranes.
2. *Long-term (chronic):* Exposure to asbestos can cause reduced pulmonary function, breathing difficulty, dry cough, broadening and thickening of the ends of the fingers, and bluish discoloration of the skin and mucous membranes.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, and morbidity and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to asbestos, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to asbestos at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include cigarette smoking, preexisting asbestos-related disease, and significant breathing impairment due to preexisting chronic lung diseases. In addition to the medical interview and physical examination, the means to identify these conditions may include the methods recommended by NIOSH and ATS.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to asbestos. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system as compared to the baseline status of the individual worker or to the expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to asbestos may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include: Scarring of the lungs (asbestosis) and its lining (pleural fibrosis) and cancer of the lungs (bronchogenic lung cancer) and its lining (mesothelioma).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to asbestos should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis for airborne asbestos may be performed by collecting asbestos fibers with membrane filters and analyzing by phase contrast microscopy. A detailed sampling and analytical method for asbestos may be found in the *NIOSH Manual of Analytical Methods* (method number 7400).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with asbestos.

SANITATION

Clothing which is contaminated with asbestos should be removed at the end of the work period and placed in nonreusable, impermeable containers for storage, transport, and disposal until it can be discarded or until provision is made for the removal of asbestos from the clothing. These containers should be marked "Asbestos-Contaminated Clothing" in easy-to-read letters. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of asbestos's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with asbestos should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle asbestos should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to asbestos may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for asbestos

Operations	Controls
During asbestos removal	Process enclosure, wet process (when possible), personal protective equipment
During the production of asbestos or the manufacture of products containing asbestos	Process enclosure, local exhaust ventilation, wet process (when possible), personal protective equipment
During the demolition of buildings	Water spray, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to asbestos, an eye wash fountain should be provided within the immediate work area for emergency use.

If asbestos gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this substance.

- **Skin exposure**

If asbestos gets on the skin, wash it immediately with soap and water.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If asbestos is spilled or leaked, the following steps should be taken:
Asbestos dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for asbestos

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ATRAZINE

INTRODUCTION

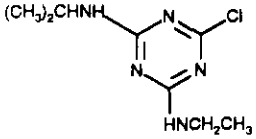
This guideline summarizes pertinent information about atrazine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8H_{14}ClN_5$

- **Structure**



- **Synonyms**

Aatrex; Atranex; Atratol A; Atred; 2-chloro-4-ethylamino-6-isopropylamino-s-triazine; 6-chloro-N-ethyl-N′-(1-methylethyl)-1,3,5-triazine-2,4-diamine; Crisatrina; Fenamin; Gesaprim; Griffex; Hungazin; Inakor; Primatol; Radazin; Shell Atrazine Herbicide; Strazine; Triazine A1294; Vectral; Weedex A; Zeazine

- **Identifiers**

1. CAS No.: 1912-24-9
2. RTECS No.: XY5600000
3. DOT UN: 2763 53
4. DOT label: Poison

- **Appearance and odor**

Atrazine is an odorless, nonflammable, colorless or white, crystalline solid. This chemical is a triazine herbicide that is available commercially as a wettable powder or a liquid emulsion and is often combined with other herbicides.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 215.72
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 1.19 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 171° to 174°C (339.8° to 345.2°F)
6. Vapor pressure at 20°C (68°F): 0.0000003 mm Hg
7. Solubility: Slightly soluble in water; soluble in diethyl ether, methanol, chloroform, dimethyl sulfoxide, ethyl acetate, and n-pentane
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat. Atrazine is very stable; it has a shelf life of several years but is slightly sensitive to natural light and extreme temperatures.
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, hydrogen chloride, and oxides of nitrogen) may be released in a fire involving atrazine.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to atrazine; this substance is not flammable.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving atrazine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving atrazine. Firefighters' protective clothing may not provide protection against permeation by atrazine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for atrazine is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned atrazine a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The OSHA and NIOSH limits are based on the risk of neuropathic and metabolic effects associated with exposure to atrazine. The ACGIH limit is based on the acute effects of exposure to atrazine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to atrazine can occur through inhalation, ingestion, or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Atrazine is an irritant of the eyes and skin in animals; at high doses, it causes nervous system effects. Eyelid edema and conjunctivitis occurred after application of atrazine to the eyes of guinea pigs, cats, and rabbits [NLM 1991]. In separate studies, it also induced severe eye irritation when applied to the eyes of rabbits [NIOSH 1991] and caused mild irritation when applied to their skin [NIOSH 1991]. The dermal LD_{50} in rabbits is 7,500 mg/kg [NIOSH 1991]. When applied to the skin of rats, atrazine caused marked erythema but no systemic toxicity [Hayes 1982]. Groups of rats that inhaled atrazine aerosol concentrations (80% wettable powder) ranging from 1,800 to 4,900 mg/m^3 for 1 hr developed no signs or symptoms of toxicity [NLM 1991]. The LC_{50} in rats is 5,200 mg/m^3 for 4 hr [NIOSH 1991]. The oral LD_{50} in mice is 1,750 mg/kg [NLM 1991]. The oral LD_{50} in rats ranges from 672 mg/kg [NIOSH 1991] to 3,080 mg/kg [NLM 1991]. Oral administration of a large amount of atrazine to rats caused them to develop muscular weakness, hypoactivity, ptosis, dyspnea, and prostration [NLM 1991]. The effects induced in rats following oral administration of the LD_{100} (3,000 mg/kg) included depression, reduced respiratory rate, motor incoordination, clonic/tonic convulsions, hypothermia, and central nervous system lesions (undefined) [NLM 1991]. Rats receiving atrazine by gavage (100, 200, or 400 mg/kg per day for 7 or 14 days) showed a dose-dependent increase in liver weight and histopathological changes in the liver [NLM 1991]. Forty percent of rats that received 20 mg/kg per day for 6 months developed bronchitis, peribronchitis, respiratory distress, pericapillary edema, and dystrophy of the brain before death [NLM 1991]. In addition, rats receiving either 10 or 50 mg/kg per day for 6 months by gavage had inhibited growth rates, leukopenia, and disturbances in vitamin metabolism [NLM 1991]. Atrazine is embryotoxic at high, maternally toxic oral doses [NLM 1991]. Some carcinogenicity bioassays with atrazine have been positive [NLM 1991]. Atrazine is mutagenic in several mammalian test systems, including human fibroblasts [NIOSH 1991; NLM 1991]. Oral administration of atrazine for up to 2 yr did not induce cancers in treated mice or rats [ACGIH 1991a; NLM 1991].

2. *Effects on Humans*: In humans, atrazine causes skin irritation [NLM 1991]. No toxicity resulted when a child ingested 800 mg or when an adult ingested 4 mg/kg [NLM 1991]. A farmer who sprayed an atrazine formulation reported a case of severe contact dermatitis; he had red, swollen hands and bloody blisters between the fingers. A patch test later showed the farmer to be sensitized to atrazine [Hayes 1982]. Atrazine may also be mutagenic in humans: lymphocytes of agricultural workers exposed to atrazine showed a statistically significant increase in the incidence of chromosomal aberrations during the spraying season [EPA 1987]. Some evidence suggests that exposure to triazine herbicides increases the risk of ovarian cancer in exposed women [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to atrazine can cause severe irritation of the eyes and mild skin irritation. Mus-

cular weakness, hypoactivity, ptosis, dyspnea, prostration, depression, reduced respiratory rate, motor incoordination, clonic/tonic convulsions, and hypothermia have also been reported in atrazine-exposed animals.

2. *Chronic exposure*: Chronic exposure of animals to atrazine has produced tissue irritation and inhibited growth rates.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of atrazine. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates, vapors, mists, or aerosols of atrazine are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if atrazine or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of atrazine may result in worker exposures to this substance:

—Use in the manufacture, formulation, or application of herbicides

—Use as a selective herbicide for control of broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, asparagus, tomato, and potato fields; macadamia orchards; conifer reforestation sites; Christmas tree plantations; and grass seed fields

—Use as a nonselective herbicide (at higher concentrations) for industrial and commercial noncropped sites such as railroads, storage yards, and highways

—Use as an algicide in lakes and ponds

—Use as a turf grass sod herbicide

The following methods are effective in controlling worker exposures to atrazine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease.

The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to atrazine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and on a history of skin allergies.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to atrazine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to atrazine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of atrazine on the skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for atrazine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne atrazine is determined by using a glass fiber filter. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 240 liters is collected. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet detector. This method is described in the OSHA Computerized Information System [OSHA 1990] and in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If atrazine contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with atrazine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of atrazine, particularly its potential for causing skin irritation.

A worker who handles atrazine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where atrazine or a solution containing atrazine is handled, processed, or stored.

STORAGE

Atrazine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of atrazine should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained atrazine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving atrazine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the atrazine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Atrazine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of atrazine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of atrazine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although atrazine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of atrazine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent skin contact with atrazine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by atrazine formulations. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to atrazine.

If atrazine is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which atrazine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with atrazine. Contact lenses should not be worn if the potential exists for atrazine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AZINPHOS-METHYL

INTRODUCTION

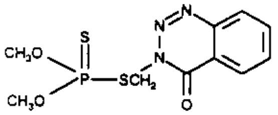
This guideline summarizes pertinent information about azinphos-methyl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{12}N_3O_3PS_2$

- **Structure**



- **Synonyms**

Guthion; methyl guthion; benzotriazine derivative of methyl dithiophosphate; benzotriazine-dithiophosphoric acid, dimethoxy ester; O-O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl] phosphoro-dithioate; Bay 9027; Bayer 9027; Carfene; Cotnion methyl; Gusathion

- **Identifiers**

1. CAS No.: 86-50-0
2. RTECS No.: TE1925000
3. DOT UN: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Azinphos-methyl is an organophosphorus pesticide. The technical product is a brown waxy solid; no data are available regarding the odor of this substance.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 317.34
2. Boiling point (at 760 mm Hg): Decomposes at temperatures above 200°C (392°F)
3. Specific gravity (water = 1): 1.44 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 73° to 74°C (163.4° to 165.2°F)
6. Vapor pressure at 20°C (68°F): 0.00038 mm Hg
7. Solubility: Slightly soluble in water; soluble in methanol, ethanol, propylene glycol, xylene, and other organic solvents
8. Evaporation rate: Negligible

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or flame.
2. Incompatibilities: Fires and explosions may result from contact of azinphos-methyl with strong oxidizers.
3. Hazardous decomposition products: Toxic gases and dusts (such as oxides of nitrogen, phosphorus, and sulfur) may be released when azinphos-methyl is heated to decomposition.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to azinphos-methyl; this substance may burn, but it does not ignite readily.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving

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azinphos-methyl; use water spray, fog, or standard foam to fight large fires involving this substance.

Fires involving azinphos-methyl should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of azinphos-methyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving azinphos-methyl. Chemical protective clothing that is specifically recommended for azinphos-methyl may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by azinphos-methyl.

EXPOSURE LIMITS

• OSHA PEL

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for azinphos-methyl is 0.2 mg/m^3 of air as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned azinphos-methyl a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek; the TLV also bears a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of anticholinesterase effects associated with exposure to azinphos-methyl.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to azinphos-methyl can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Azinphos-methyl is a cholinesterase inhibitor in animals that is capable of inducing death from respiratory arrest. Significant dermal absorption can occur in animals. The dermal LD_{50} is about 65 mg/kg in mice and 220 mg/kg in rats [NIOSH 1991]. Among rats that inhaled an aerosol of technical grade product containing 72% to 73% azinphos-methyl, the 1-hr LC_{50} was approximately 75 mg/m^3 (69 mg/m^3 for males and 79 mg/m^3 for females). The signs and symptoms of toxic cholinesterase inhibition included salivation, lacrimation, exophthalmos, defecation, urination, and muscle fasciculations before respiratory failure and death [NIOSH 1991; SRI 1978]. The oral LD_{50} was 15 mg/kg in mice and 7 mg/kg in rats [NIOSH 1991]. Rats that inhaled azinphos-methyl at 4.72 mg/m^3 for 12 weeks (6 hr/day, 5 days/week) showed a significant reduction in erythrocyte and plasma cholinesterase activity [Proctor et al. 1988]. Rats tolerated a dietary concentration of 5 ppm for 60 days without cholinesterase inhibition; at 20 ppm for 60 days, however, brain and red blood cell cholinesterase levels were inhibited by as much as 30% [ACGIH 1991a]. When azinphos-methyl was administered to pregnant mice and rats, it caused no adverse developmental effects in the offspring [NIOSH 1991; NLM 1991]. A National Cancer Institute study provided equivocal evidence that oral dosing of male rats with azinphos-methyl causes cancer of the thyroid and pancreas; this substance was not shown to be carcinogenic in female rats or in male or female mice [NCI 1978].

2. *Effects on Humans*: Azinphos-methyl is a cholinesterase inhibitor in humans. Eight workers engaged in the formulation of a wettable azinphos-methyl powder were exposed to concentrations as high as 9.6 mg/m^3; blood serum levels in some workers were depressed to 78% of their pre-exposure baseline cholinesterase levels [Proctor et al. 1988]. In a group of male agricultural workers working in a field that had been treated with azinphos-methyl, the mean red blood cell cholinesterase activity was significantly below that of workers engaged in an untreated field [NLM 1991]. Volunteers ingesting 4 to 20 mg azinphos-methyl/day for 30 days did not show a drop in cholinesterase levels [ACGIH 1991a].

• Signs and symptoms of exposure

1. *Acute exposure*: The following signs and symptoms of acute exposure to azinphos-methyl vary with the route of entry and the degree of exposure [NLM 1991]. Effects associated with inhalation exposure include a feeling of

tightness in the chest, wheezing, bronchoconstriction, excessive bronchial secretion, laryngeal spasms, excessive salivation, cyanosis, miosis, pain in and between the eyes, blurring of distant vision, tearing, rhinorrhea, and frontal headache. Within 15 to 120 min of ingestion, gastrointestinal effects appear—anorexia, nausea, vomiting, abdominal cramps, and diarrhea. After skin absorption, sweating and muscle twitching occur in the area of skin contact. If overexposure by any route is severe, signs and symptoms include muscular weakness, involuntary twitching, and eventually paralysis. The most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. Blood pressure may fall, and cardiac irregularities (including complete heart block) may occur; these effects are sometimes reversible if adequate pulmonary ventilation is established. Unless the exposure is lethal, complete symptomatic recovery usually occurs within 1 week; however, increased susceptibility to the effects of anticholinesterase agents usually persists for several weeks after exposure.

2. *Chronic exposure*: Repeated exposure to azinphos-methyl at concentrations below those that will cause symptoms after a single exposure can cause the same signs and symptoms as acute exposure.

- **Emergency procedures**

[illegible]

[illegible]

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Azinphos-methyl can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of azinphos-methyl are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if azinphos-methyl or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations involve azinphos-methyl and may result in worker exposures to this substance:

—Manufacture, formulation, and application of azinphos-methyl as an insecticide and acaricide on field crops, fruits, vegetables, cotton, tobacco, nuts, sugar cane, soybeans, ornamentals, grasses, and trees

—Use of azinphos-methyl as an additive in the food and drinking water of animals

The following methods are effective in controlling worker exposures to azinphos-methyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to azinphos-methyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A baseline red blood cell acetylcholinesterase level should be established for each potentially exposed worker.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to azinphos-methyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with decreases in blood cholinesterase activity.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to azinphos-methyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of azinphos-methyl on blood cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Red blood cell cholinesterase activity can be measured to monitor both acute and chronic exposure to azinphos-methyl. A worker should be removed from exposure if his or her erythrocyte cholinesterase level drops to or below 40% of the pre-exposure baseline value for that individual; he or she should not be allowed to return to work until this level has again reached 80% of the pre-exposure baseline level.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Neither NIOSH nor OSHA has a validated method for sampling azinphos-methyl in the workplace. However, the following secondary analytical method, which has not been validated, is available.

A worker's exposure to airborne azinphos-methyl is determined by using a specially designed tube called an OSHA versatile sampler (OVS-2) containing XAD-2 resin (270/140-mg sections, 20/60 mesh) and a glass fiber filter. Samples are collected at a recommended flow rate of 1 liter/min until a recommended air volume of 480 liters is collected. The sample is desorbed with toluene. Analysis is conducted by gas chromatography using a flame photometric detector and an OV-1 column at 175°C (347°F). The limit of detection for this procedure is 5 µg/sample. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

Because azinphos-methyl can be deadly if absorbed through the skin, an exposed worker should remove any contaminated clothing immediately and flush the affected areas with copious amounts of water for 15 min; the worker should then wash thoroughly with soap and water. At the end of the day, workers who handle azinphos-methyl or liquid containing azinphos-methyl should use soap and water to wash any areas of the body that may have contacted this pesticide, even if none is detected on the skin.

Clothing and shoes contaminated with azinphos-methyl should be removed immediately; speed in removing these articles is essential. Persons laundering contaminated clothing should be informed of the hazardous properties of azinphos-methyl, particularly its potential for being absorbed through the skin.

A worker who handles azinphos-methyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where azinphos-methyl or a solution containing it is handled, processed, or stored.

STORAGE

Azinphos-methyl should be stored in a cool, dry, well-ventilated area in tightly sealed original containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of azinphos-methyl should be protected from physical damage and should be separated from oxidizers, heat, sparks, and open flame. Azinphos-methyl should never be stored near any type of food. Because containers that formerly contained azinphos-methyl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving azinphos-methyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the atmosphere to reduce the concentration.
4. Use water spray to reduce vapors.
5. For dry spills (azinphos-methyl in solid form), use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
6. Absorb small liquid spills (azinphos-methyl formulations) with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the azinphos-methyl for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 10,000 lb or more of azinphos-methyl onsite must comply with EPA's emergency planning requirements [40 CFR 355.30]. (The employer must comply with these requirements if azinphos-methyl is in the form of a finely divided powder or is handled in solution or in molten form, and if 10 lb or more is present at the facility.)

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for azinphos-methyl is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of azinphos-methyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although azinphos-methyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of azinphos-methyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with azinphos-methyl. Gloves, overalls, and boots should be worn when handling azinphos-methyl or any organophosphorus pesticide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by azinphos-methyl and may provide protection for periods greater than 8 hr: neoprene and nitrile rubber. Natural rubber and polyvinyl chloride have demonstrated questionable resistance to permeation by azinphos-methyl.

If azinphos-methyl is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which azinphos-methyl might contact the eyes (e.g., through dust particles, mists, or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with azinphos-methyl. Contact lenses should not be worn if the potential exists for azinphos-methyl exposure.

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Occupational Health Guideline for Soluble Barium Compounds (as Barium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble barium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Barium nitrate

- Formula: $Ba(NO_3)_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium oxide

- Formula: BaO
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium carbonate

- Formula: $BaCO_3$
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium chloride

- Formula: $BaCl_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble barium compounds is 0.5 milligram of soluble barium compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble barium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Soluble barium compounds may cause local irritation of the eyes, nose, throat, bronchial tubes, and skin. Soluble barium compounds may also cause severe stomach pains, slow pulse rate, irregular heart beat, ringing of the ears, dizziness, convulsions, and muscle spasms. Death may occur.
2. *Long-term Exposure:* None known
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble barium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble barium compounds at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the heart, lungs, and nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Soluble barium compounds cause human lung damage. Surveillance of the lungs is indicated.

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—FVC and FEV (1 sec): Soluble barium compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Electrocardiogram: Barium compounds may cause cardiac arrhythmias and may have a direct effect on the cardiac muscle. Periodic surveillance of the heart is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Soluble barium salts cause severe gastroenteritis and systemic effects by ingestion. Intravenous injection of barium compounds in animals causes a strong, prolonged stimulation of muscle resulting in hyperperistalsis, bladder contraction, vasoconstriction, and irregular contraction of the heart followed by arrest in systole. Animals also exhibit stimulation of the central nervous system followed by paralysis. Ingestion of barium carbonate by humans causes gastroenteritis, muscular paralysis, slow pulse rate, extrasystoles, and hypokalemia. Heavy industrial exposure to dusts of barium sulfate or barium oxides may produce a benign pneumoconiosis, termed baritosis. It results in no impairment of ventilatory function, although signs of mild bronchial irritation may occur. Characteristic x-ray changes are those of small, dense, circumscribed nodules evenly distributed throughout the lung fields, reflecting the radio-opacity of the barium dust. Bronchial irritation has been reported from the inhalation of barium carbonate dust. Barium hydroxide and barium oxide are strongly alkaline in aqueous solution, causing severe burns of the eye and irritation of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Barium nitrate**

1. Molecular weight: 261.4
2. Boiling point (760 mm Hg): Greater than 592 C (greater than 1098 F) (decomposes)
3. Specific gravity (water = 1): 3.24
4. Vapor density (air = 1 at boiling point of barium nitrate): Not applicable
5. Melting point: 592 C (1098 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 9.2
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Barium oxide**

1. Molecular weight: 153.3
2. Boiling point (760 mm Hg): 2000 C (3632 F)
3. Specific gravity (water = 1): 5.72
4. Vapor density (air = 1 at boiling point of barium oxide): Not applicable
5. Melting point: 1921 C (3490 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Barium carbonate**

1. Molecular weight: 197.3
2. Boiling point (760 mm Hg): 1300 C (2372 F) (decomposes)
3. Specific gravity (water = 1): 4.25
4. Vapor density (air = 1 at boiling point of barium carbonate): Not applicable
5. Melting point: Decomposes at 1300 C (2372 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0022
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Barium chloride**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 1560 C (2840 F)
3. Specific gravity (water = 1): 3.86
4. Vapor density (air = 1 at boiling point of barium chloride): Not applicable
5. Melting point: 963 C (1765 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 36
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: For barium nitrate, elevated temperatures may cause melting and decomposition; for the other compounds, none hazardous.
2. Incompatibilities: Contact of barium oxide with water, carbon dioxide, or hydrogen sulfide may cause fires and explosions. Contact of barium carbonate with acids causes formation of carbon dioxide gas that may cause suffocation in enclosed spaces. Contact of barium nitrate with organic matter and combustible materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving barium nitrate.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For barium nitrate, data not available; for the the other compounds, not applicable.
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Large amounts of water should be used on adjacent fires.

- **Warning properties**

According to Grant, barium chloride causes "considerable iritis, which subsides in a few days" when "tested in neutral 0.08 to 0.1 M solution on rabbit eyes by injection into the cornea or by dropping for 10 minutes on the eye after the corneal epithelium was removed to facilitate penetration." Grant states that "both the oxide and hydroxide are capable of causing severe alkali burns of the eye, similar to those produced by calcium hydroxide."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by leaching in hot water, solution of sample in acid, and analysis in an atomic absorption spectrophotometer. An analytical method for soluble barium compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with barium oxide or liquids containing barium oxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where exposure of an employee's body to barium oxide or liquids containing barium oxide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of barium oxide or liquids containing barium oxide contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to barium oxide or liquids containing barium oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with barium oxide or liquids containing barium oxide should wash any areas of the body which may have contacted barium oxide at the end of each work day.
- Skin that becomes contaminated with barium carbonate, barium chloride, or barium nitrate should be promptly washed or showered to remove any contaminant. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

- Skin that becomes contaminated with barium oxide should be promptly washed or showered to remove any barium oxide from the skin after all obvious amounts of barium oxide have been removed by other means (e.g., by use of oil or vaseline). Employees who are being burned by barium oxide should immediately utilize quick drenching facilities without first removing barium oxide by other means.
- Eating and smoking should not be permitted in areas where solid barium carbonate, barium chloride, barium nitrate, or barium oxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble barium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and distribution of soluble barium compounds	Process enclosure; local exhaust ventilation
Use in manufacture of pressed and blown glasssware and flint and crown optical glass; manufacture of ceramic products; use in electronics industry in manufacture of magnets, vacuum tubes, cathodes, x-ray fluorescent screens, TV picture tubes, and dry cell depolarizers	Process enclosure; local exhaust ventilation
Use in manufacture of photographic papers, dyes, and chemicals	Process enclosure; local exhaust ventilation
Use as pesticides, rodenticides, and disinfectants; use in manufacture of explosives, matches, and pyrotechnics as igniter compositions and fireworks	Process enclosure; local exhaust ventilation
Use as an additive in manufacture of grease, and manufacture of lubricating oils; use in refining of vegetable and animal oils	Process enclosure; local exhaust ventilation
Use in case-hardening of steel in metallurgy; in welding aluminum; in electroplating; and in aluminum and sodium refining	Process enclosure; local exhaust ventilation
Use in water treatment and boiler compounds for softening water; use as catalysts, analytical reagents, and purifying agents	Process enclosure; local exhaust ventilation
Use for treatment of textiles, leather, and rubber; use in manufacture of paper and cellulose as a bleaching agent; use in manufacture of pigments, colors, and lakes	Process enclosure; local exhaust ventilation
Use as a depilatory in processing of hides; as a fire-proof and extinguishing agent; in embalming; in sugar refining; in gas and solvent drying; in marble substitutes; in valve manufacture; and as a smoke suppressant in diesel fuels	Process enclosure; local exhaust ventilation
Use in manufacture of pigments, paints, enamels, and printing inks	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solutions of barium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solutions of barium compounds get on the skin, immediately flush the contaminated skin with water. If solutions of barium compounds soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble barium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble barium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble barium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble barium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble barium compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR SOLUBLE BARIUM COMPOUNDS (AS BARIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 250 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BARIUM SULFATE

INTRODUCTION

This guideline summarizes pertinent information about barium sulfate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$BaSO_4$

- **Synonyms**

Actybaryte; artificial barite; artificial heavy spar; bakontal; baridol; barite; barosperse; barotrast; baryta white; barytes; bayrites; citobaryum; colonatrast; finemeal; liquibarine; macropaque; neobar; oratrast; permanent white; precipitated barium sulphate; raybar; redi-flow; solbar; sulfuric acid, barium salt (1:1); supramike; travad; unibaryt

- **Identifiers**

1. CAS No.: 7727-43-7
2. RTECS No.: CR0600000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Barium sulfate is a heavy, noncombustible, white or yellowish, odorless powder or crystalline solid. It occurs naturally as the mineral barite and can also be manufactured. Barium sulfate is available in several commercial grades, including technical, dry, pulp, bleached, ground, floated, natural, pharmaceutical, and X-ray.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 233.42
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.25 to 4.50 at 20°C (68°F)
4. Vapor density: Not applicable.
5. Melting point: 1,580°C (2,876°F); decomposes above 1,600°C (2,912°F)
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Almost insoluble in water, dilute acids, or alcohol; soluble in hot concentrated sulfuric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Explosions may result from contact of barium sulfate with aluminum in the presence of heat.
3. Hazardous decomposition products: Toxic gases and particulates (such as sulfur oxides or barium fumes) may be released in a fire involving barium sulfate.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to barium sulfate; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving barium sulfate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of barium sulfate may

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Public Health Service Centers for Disease Control
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explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Do not scatter this material. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving barium sulfate. Chemical protective clothing that is specifically recommended for barium sulfate may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by barium sulfate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for barium sulfate is 10 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr TWA concentrations [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned barium sulfate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye, nose, and upper respiratory tract irritation and pneumoconiosis associated with exposure to barium sulfate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to barium sulfate can occur through inhalation and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Barium sulfate dust is a mechanical irritant. Rats exposed to a 40-mg/m^3 concentration of barium sulfate dust for 5 hr/day during a 2-month period did not show adverse effects [ACGIH 1991a]. In another study, rats inhaling barium sulfate dust (concentration not specified) developed a reversible pneumoconiosis without fibrosis [NLM 1991]. Intratracheal injection of radioactive barium sulfate caused bronchogenic carcinomas in rats [Clayton and Clayton 1981].

2. *Effects on Humans*: Inhalation of barium sulfate causes physical irritation and a benign pneumoconiosis (known as baritosis) in humans. In Italy, Germany, Czechoslovakia, and the United States, workers exposed to the fine dust of barium sulfate have developed a benign, noncollagenous form of pneumoconiosis that generally disappears when exposure ceases. Although chronic bronchial irritation occasionally persists after termination of exposure, no adverse effects on pulmonary function have been reported [Clayton and Clayton 1981; NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to barium sulfate can cause redness and itching of the eyes and nose and a scratchy throat. No other acute effects have been reported.

2. *Chronic exposure*: Chronic exposure to barium sulfate can cause radiographic evidence of disseminated, discrete nodular opacities in the lung fields; in most cases, these opacities disappear after cessation of exposure. Chronic bronchial irritation has been reported occasionally in baritotic workers.

• Emergency procedures

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Seek medical attention if signs and symptoms of toxicity develop, or take the following steps if a large amount of barium sulfate is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a fluid such as water.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve barium sulfate and may result in worker exposures to this substance:

—Mining, grinding, and bagging of barite and manufacture of barium sulfate

—Use of barium sulfate in oil-drilling muds, as a filler and delustrant for textiles, and as an expander in battery plate pastes

—Manufacture of lithopane, a white pigment

—Use of barium sulfate as a source of other barium compounds

—Manufacture of photographic papers, glass, ceramics, artificial ivory, cellophane, filler for rubber, linoleum, oil cloth, polymeric fibers and resins, and lithographic inks

—Use of barium sulfate as a diagnostic aid and X-ray contrast medium

—Use of barium sulfate as a watercolor pigment for colored paper and wallpaper, as an agent for modifying the colors of other pigments, and as an ingredient in the heavy concrete used for radiation shielding

The following methods are effective in controlling worker exposures to barium sulfate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to barium sulfate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to barium sulfate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to barium sulfate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of barium sulfate on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for barium sulfate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne barium sulfate is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5-micron) to measure both total dust and the respirable fraction (a 10-mm nylon cyclone must be used for collecting the respirable fraction). Samples are collected at a maximum flow rate of 2 liters/min (total dust) or 1.7 liters/min (respirable fraction) until a maximum air volume of 960 liters (total dust) or 816 liters (respirable fraction) is collected. Gravimetric analysis is conducted by weighing the filters. This method has a sampling and analytical error of 0.10 and is described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985] and in the OSHA Computerized Information System (respirable fraction and total dust) [OSHA 1990]. A similar method is described in Method 500 (Nuisance dust, total) and Method 600 (Nuisance dust, respirable) of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If barium sulfate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with barium sulfate should be removed to prevent physical irritation of the skin.

A worker who handles barium sulfate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where barium sulfate is handled, processed, or stored.

STORAGE

Barium sulfate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of barium sulfate should be protected from physical damage and should be stored separately from aluminum, heat, sparks, and open flame. Because containers that formerly contained barium sulfate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving barium sulfate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

5. For small, dry spills, use a clean shovel and place the material into a clean, dry, covered container; remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Barium sulfate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.30] to notify the National Response Center of an accidental release of barium sulfate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Facilities in SIC codes 20 to 39 who employ 10 or more workers and who manufacture more than 25,000 lb of barium compounds (including barium sulfate) per calendar year or who use more than 10,000 lb of barium compounds per calendar year are required to comply with EPA requirements in 40 CFR 372 that mandate the submission of Toxic Chemical Release Inventory Forms.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although barium sulfate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing more information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of barium sulfate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn if necessary to prevent skin contact with barium sulfate (gloves, boots, aprons, and gauntlets).

Safety glasses, goggles, or face shields should be worn during operations in which barium sulfate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with barium sulfate. Contact lenses should not be worn if the potential exists for barium sulfate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENOMYL

INTRODUCTION

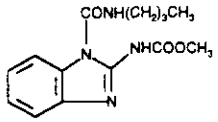
This guideline summarizes pertinent information about benomyl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{14}H_{18}N_4O_3$

- **Structure**



- **Synonyms**

1-(Butylcarbamoyl)-2-benzimidazolecarbamic acid; methyl ester; 1-(butylcarbamoyl)-2-benzimidazol-methylcarbamat; 1-(n-butylcarbamoyl)-2-(methyoxy-carboxamido)-benzimidazol; carbamic acid; methyl 1-(butylcarbamoyl)-2-benzimidazole ester; Benlate; Arilate; BBC; Benlate 50; Benomyl 50W; BNM; Fundasol; Fungicide 1991; MBC; Tersan 1991

- **Identifiers**

1. CAS No.: 17804-35-2
2. RTECS No.: DD6475000
3. DOT UN: 2757 55 (carbamate pesticide, solid, not otherwise specified)
4. DOT label: Poison or St. Andrew's Cross (depending on quantity shipped)

- **Appearance and odor**

Benomyl is a noncombustible, white, crystalline solid that decomposes without melting. It has a faint, acrid odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 290.32
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: Decomposes without melting above 300°C (572°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg
7. Solubility: Very slightly soluble in water; soluble in ethanol, heptane, xylene, acetone, dimethylformamide, and chloroform
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, water, strong acids, and strong alkalies can cause benomyl to decompose.
2. Incompatibilities: None reported
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving benomyl.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating to benomyl; this substance is not combustible.

1. Flash point: Not applicable

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving benomyl.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benomyl is 10 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has no recommended exposure limit (REL) for benomyl [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned benomyl a threshold limit value (TLV) of 10 mg/m^3 (0.84 ppm) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The OSHA limit is based on the risk of physical irritation, erythema, and potential reproductive effects associated with exposure to benomyl; the ACGIH limit is based on the low toxicity of this substance.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to benomyl can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Benomyl is a skin sensitizer, reproductive toxin, and teratogen in animals. When instilled into the eyes of rabbits, dry benomyl powder (50%) or 0.1 ml of a 10% benomyl solution produced only temporary, mild irritation of the conjunctiva [ACGIH 1991a]. When applied to the intact, shaved skin of guinea pigs, a benomyl concentration of 25% in a 50% wettable powder produced reddened skin in 1 of 10 animals; lower concentrations of benomyl did not cause skin irritation [ACGIH 1991a]. Benomyl caused mild to moderate skin sensitization in guinea pigs injected intradermally with benomyl and then challenged by topical application [Clayton and Clayton 1981]. The dermal LD$_{50}$ in rabbits is greater than 10 g/kg [ACGIH 1991a]. The LC$_{50}$ in rats is greater than 2,000 mg/m^3 for 4 hr. The oral LD$_{50}$ in rats is 10 g/kg [NIOSH 1991]. Rats exposed to 100 mg/m^3 for 4 hr/day, 5 days/week for 3 weeks developed neither clinical or histopathological effects [NLM 1991]. Rats exposed to technical-grade benomyl at 10, 50, or 200 mg/m^3 for 6 hr/day, 5 days/week for 14 weeks had suppressed food consumptions and body weight gains at the highest level. Only the 50- and 200-mg/m^3 exposures induced any effect (a degeneration of the olfactory epithelium) after 45 days. Oral administration of benomyl (2,500 mg/kg in the diet) to rats for 90 days did not cause toxicity, but rats and dogs fed benomyl for 2 years exhibited a low order of toxicity (undefined) [NLM 1991].

A number of studies [Barnes et al. 1983; Carter et al. 1984; Ellis et al. 1987] have demonstrated benomyl's reproductive and teratogenic effects. Adult rats fed benomyl for 70 days showed significant depressions in sperm count and testicular weight and had lowered fertility indexes [Barnes et al. 1983]. Similar effects were elicited in rats given benomyl during or after puberty [Carter et al. 1984]. Rats intubated with benomyl doses ranging from 125 to 500 mg/kg per day during the first 20 days of pregnancy produced offspring with dose-related increases in the rates of skull and central nervous system anomalies [NLM 1991]. In addition, pregnant mice administered 1,100 mg/kg benomyl on days 7 to 17 of pregnancy had offspring with similar abnormalities [NIOSH 1991]. In another study, the offspring of rats given 31.2, 62.5, or 125 mg/kg by gavage on days 7 to 21 of gestation showed a dose-dependent increase in the incidence of craniocerebral and systemic malformations; an increase in fetal resorptions and late fetal deaths also occurred in the offspring of animals in the high-dose group [Ellis et al. 1987]. Although benomyl is mutagenic in bacterial test systems [NIOSH 1991], it did not induce cancer in either rats or dogs fed the compounds for two years [NLM 1991].

2. *Effects on Humans*: Benomyl is an irritant and skin sensitizer in humans. A recent U.S. study showed that two migrant workers in a group of farm workers with dermatitis had positive responses to 0.1% benomyl solutions in patch tests, indicating that they had become sensitized to this substance [Schuman and Dobson 1985]. A field study in Japanese farmers showed that 20% of women farmers had positive patch tests to benomyl as well as cross-sensitivities to other pesticides [Matsushita and Aoyama 1981]. Irritation, erythema, salivation, sweating, lassitude, reproductive effects, muscular incoordination, nausea, vomiting, abdominal cramps, angina pectoris, central nervous system depression, and cholinesterase inhibition have been reported [NLM 1991]. Benomyl is mutagenic in human in vitro test systems [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to benomyl dust can cause irritation, erythema, salivation, sweating, lassitude, reproductive effects, muscular incoordination, nausea, vomiting, abdominal cramps, angina pectoris, central nervous system depression, and cholinesterase inhibition.

2. *Chronic exposure*: Chronic exposure to benomyl may cause skin sensitization with irritation, redness, and cholinesterase inhibition.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for seriously affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of benomyl. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of benomyl are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if benomyl or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve benomyl and may result in worker exposures to this substance:

—Manufacture and formulation of pesticides containing benomyl

—Use of benomyl as a systemic fungicide and ascaricide

—Use of benomyl in veterinary medicine as an anthelmintic

—Use of benomyl as an oxidizer in sewage treatment

The following methods are effective in controlling worker exposures to benomyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers

for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to benomyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to benomyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or other diseases of the skin. On the basis of effects seen in animals, men and women who plan to have children should be advised that they may be at increased risk of having a child with birth defects, and men should be advised that they may be at increased risk of experiencing adverse reproductive effects.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to benomyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benomyl on the skin and the male reproductive system. Men and women who plan to have children should again be advised that they may be at increased risk of having a child with birth defects. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for benomyl.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benomyl is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by high-performance liquid chromatography. This method is described in the OSHA Computerized Information System [OSHA 1989].

PERSONAL HYGIENE

If benomyl contacts the skin, workers should wash the affected areas with soap and water.

Clothing and shoes contaminated with benomyl should be removed, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of benomyl.

A worker who handles benomyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where benomyl or a solution containing benomyl is handled, processed, or stored.

STORAGE

Benomyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of benomyl should be protected from physical damage and should be stored separately from strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained benomyl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving benomyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For dry spills, use a vacuum or a wet method to reduce dust dispersion and place the material into a clean, dry container; cover and remove the container from the spill area.
5. Absorb liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Benomyl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of benomyl; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benomyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although benomyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benomyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with benomyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to benomyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to benomyl.

If benomyl is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which benomyl might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benomyl. Contact lenses should not be worn if the potential exists for benomyl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
BENZENE
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about benzene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_6H_6
- **Structure:**

- **Synonyms:** Benzol, benzole, benzolene, bicarburet of hydrogen, carbon oil, coal naphtha
- **Identifiers:** CAS 71-43-2; RTECS CY1400000; DOT 1114, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with an aromatic odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 78.12
2. Boiling point (at 760 mmHg): 80.1°C (176°F)
3. Specific gravity (water = 1): 0.88
4. Vapor density (air = 1 at boiling point of benzene): 2.7
5. Melting point: 5.5°C (42°F)
6. Vapor pressure at 20°C (68°F): 75 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.06
8. Evaporation rate (butyl acetate = 1): 5.1
9. Saturation concentration in air (approximate) at 25°C (77°F): 12.5% (125,000 ppm)
10. Ionization potential: 9.25 eV

- **Reactivity**

Incompatibilities: Benzene reacts with strong oxidizers including chlorine, oxygen, and bromine with iron.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving benzene.
3. Caution: Benzene will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -11.1°C (12°F) (closed cup)
2. Autoignition temperature: 498°C (928°F)
3. Flammable limits in air, % by volume: Lower, 1.4; upper, 7.1
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical extinguishants are effective. Water may be an ineffective extinguishant but may be used to cool fire-exposed containers.
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Unusual fire and explosion hazards: Benzene liquid is flammable, and its vapors can easily form explosive mixtures. Flashbacks may occur along a vapor trail.

- **Warning properties**

1. Odor threshold: 12 ppm
2. Eye irritation levels: 3,000 ppm for 0.5-1 hour
3. Other information: 3,000 ppm may irritate nose and respiratory tract.
4. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzene is 1 part of benzene per million parts of air (PPM) as a time-weighted average (TWA) concentration over an 8-hour workshift; the short-term exposure limit is 5 ppm in any 15-minute sampling period. The National Institute for Occupational Safety and Health (NIOSH) recommends that benzene be controlled and handled as a potential human carcinogen in the workplace and that exposure be reduced to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 ppm [0.32 milligrams of benzene per cubic meter of air (mg/m^3)] as an 8-hour TWA and 1 ppm (3.2 mg/m^3) as a ceiling in any 15-minute sampling period. The NIOSH REL is the lowest con-

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centration detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated benzene as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 10 ppm (30 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for benzene

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	1	—
Short-term exposure limit (15 min)	5	—
NIOSH REL (Ca)* TWA	0.1	0.32
Ceiling (15 min)	1	3.2
ACGIH TLV® TWA (A2)†	10	30

* (Ca): NIOSH recommends treating as a potential human carcinogen.
†(A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Benzene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of benzene by rats, mice, or rabbits caused narcosis, spontaneous heart contractions (ventricular fibrillation), and death due to respiratory paralysis. Subchronic inhalation of benzene by rats produced decreased white blood cell counts, decreased bone marrow cell activity, increased red blood cell activity, and cataracts. In rats, chronic inhalation or oral administration of benzene produced cancers of the liver, mouth, and Zymbal gland. Inhalation of benzene by pregnant rats caused retardation of fetal development and increased fetal mortality.
2. *Effects on humans:* Acute inhalation exposure of benzene has caused nerve inflammation (polyneuritis), central nervous system depression, and cardiac sensitization. Chronic exposure to benzene has produced anorexia and irreversible injury to the blood-forming organs; effects include aplastic anemia and leukemia.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to benzene can cause dizziness, euphoria, giddiness, headache, nausea, staggering gait, weakness, drowsiness, respiratory irritation, pulmonary edema and pneumonia, gastrointestinal irritation, convulsions, and paralysis. Benzene can also cause irritation to the skin, eyes, and mucous membranes.
2. *Long-term (chronic):* Exposure to benzene can cause fatigue, nervousness, irritability, blurred vision, and labored breathing. Repeated skin contact can cause redness, blistering, and dry, scaly dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to benzene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems. The physician should obtain baseline values for the complete blood count and a stained differential count of all blood cell types. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzene at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease, concurrent dermatitis, or mild non-hemolytic anemia (e.g., mild iron-deficiency anemia).

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to benzene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination.**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to benzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Acute myeloid leukemia and contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Decrease in the number (neutropenia) or absence (agranulocytosis) of certain white blood cells in the peripheral circulation and/or in the bone marrow (aplastic anemia) and cancer of the red blood cells (erythroleukemia).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to benzene should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzene. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting benzene vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure benzene may also be used if available. A detailed sampling and analytical method for benzene may be found in the *NIOSH Manual of Analytical Methods* (method number 1500).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with benzene.

SANITATION

Clothing which is contaminated with benzene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of benzene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with benzene should be promptly washed with soap and water.

Workers who handle benzene should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzene may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for benzene

Operations	Controls
During the manufacture and processing of benzene; during use as a raw material in the production of aromatic compounds and derivatives	Process enclosure, local exhaust ventilation, personal protective equipment
During the use of chemicals in which benzene may be an impurity (e.g., naphthas, toluene, xylene)	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture and use of motor fuel blends in which benzene is used as an ingredient; during use as an extracting solvent	Process enclosure (when possible), local exhaust ventilation, personal protective equipment, material substitution
During the preparation and use of paint and varnish removers, rubber cements, and lacquers	Process enclosure (when possible), local exhaust ventilation, personal protective equipment, material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to benzene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If benzene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to benzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzene gets on the skin, wash it immediately with soap and water. If benzene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If benzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing benzene, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing benzene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing benzene may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for benzene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZIDINE

INTRODUCTION

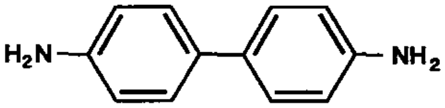
This guideline summarizes pertinent information about benzidine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{12}N_2$

- **Structure**



- **Synonyms**

1,1'-Biphenyl-4,4'-diamine, 4,4'-diaminobiphenyl, 4,4'-biphenyldiamine, 4,4'-bianiline, C.I. Azoic Diazo Component 112, Fast Corinth base B, p-diaminodiphenyl

- **Identifiers**

1. CAS No.: 92-87-5
2. RTECS No.: DC9625000
3. DOT UN: 1885 53
4. DOT label: Poison

- **Appearance and odor**

Benzidine is a white, gray-yellow, or slightly reddish crystalline solid or powder that has no odor. Benzidine is no longer manufactured commercially in the United States, although this substance is still used as an intermediate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 184.2
2. Boiling point (at 760 mm Hg): 400°C (752°F)
3. Specific gravity (water = 1): 1.25 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of benzidine): 6.36
5. Melting point: 115°C (239°F)
6. Vapor pressure at 20°C (68°F): Quantitative data are not available, but vapor pressure is reported to be low.
7. Solubility: Slightly soluble in cold water; soluble in hot water, alcohol, and ether
8. Evaporation rate: Data not available

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- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: Contact of benzidine with red fuming nitric acid may cause a fire.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, carbon monoxide, and benzidine vapors) may be released when benzidine is heated to decomposition.
  4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for benzidine. Benzidine may burn, but it does not ignite readily.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving benzidine.

Fires involving benzidine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Containers of benzidine should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving benzidine. Structural firefighters' protective clothing may provide limited protection against fires involving benzidine.

EXPOSURE LIMITS

- **OSHA PEL**

Because benzidine is a recognized occupational carcinogen, the Occupational Safety and Health Administration (OSHA) standard for benzidine does not have a numerical permissible exposure limit (PEL); instead, the standard regulates the industrial use of benzidine by requiring implementation of stringent controls wherever benzidine or solid or liquid mixtures containing 0.1% or more benzidine by weight or volume are manufactured, processed, repackaged, released, handled, or stored. This standard is codified at 29 CFR 1910.1010.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers benzidine a potential human carcinogen and recommends that the above standard [29 CFR 1910.1010] be followed [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated benzidine as an A1 substance (recognized human carcinogen). The ACGIH has also assigned benzidine a Skin notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The OSHA, ACGIH, and NIOSH limits are based on the risk of bladder and other cancer associated with exposure to benzidine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to benzidine can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Benzidine is a liver toxin and a potent carcinogen in experimental animals; in carcinogencity bioassays, this substance caused tumors of the liver, mammary gland, Zymbal gland, colon, and bladder in animals of several species. The oral LD_{50} in rats is 309 mg/kg [NIOSH 1993]. The oral LD_{50} in mice is 214 mg/kg [NIOSH 1993]. Benzidine has been tested for carcinogenicity in mice, rats, and hamsters by oral administration; in mice and rats by subcutaneous administration; and in rats by inhalation and by intraperitoneal administration. Except by

inhalation, benzidine caused increased incidences in tumors, both benign and malignant, in at least one sex of animal in all species tested. Oral administration in dogs also caused bladder cancers [IARC 1982]. With activation, benzidine is mutagenic in bacterial test systems [NIOSH 1993; IARC 1982]. The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence that benzidine is an animal carcinogen [IARC 1982].

2. *Effects on Humans:* Numerous case reports and epidemiological studies in workers from many countries, including the United States, have shown that benzidine is a potent carcinogen, causing papillomas and carcinomas of the urinary tract, and especially of the urinary bladder [IARC 1972; IARC 1982]. The latency period for benzidine tumors is 2 to 42 years, with an average latency of 16 years [Proctor et al. 1988]. In one U.S. dye manufacturing facility, bladder tumors developed in 36 workers who had been exposed to benzidine over a 45-year period (1930 to 1975) [IARC 1982]. In another group of 25 U.S. workers engaged in benzidine manufacture, 13 employees were found to have bladder tumors; all five of the workers in this group who had been exposed to benzidine for more than 15 years developed bladder tumors. Airborne benzidine concentrations at this plant were estimated to have ranged from 0.005 to 17.6 mg/m^3 [IARC 1982]. An increase in the number of sister chromatid exchanges has also been reported in workers exposed to benzidine [IARC 1982]. The International Agency for Research on Cancer has concluded that there is sufficient evidence that benzidine is a human carcinogen [IARC 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms for acute inhalation or dermal exposures have been reported. However, ingestion has caused nausea, vomiting, headache, mental confusion, dizziness, vertigo, methemoglobinemia, increase in the number of white blood cells, and Heinz bodies.

2. *Chronic exposure*: Chronic exposure to benzidine may cause blood in the urine (seen microscopically in early disease) and frequent and painful urination. The onset of bladder tumors may go undetected, and the disease may be in an advanced stage before any signs or symptoms appear. Despite aggressive treatment, tumors frequently recur.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of benzidine. Benzidine can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and thoroughly wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of benzidine are inhaled, move the victim to fresh air *immediately.* Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if benzidine or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve benzidine and result in worker exposures to this substance:

—Use as an intermediate in the preparation of azo dyes and pigments

—Formerly used in forensic medicine to detect blood and other substances

—In declining use in security printing and as a stiffening agent in rubber compounding

—In declining use as a laboratory reagent

The only method that is effective in controlling worker exposures to benzidine is:

—Process enclosure

This substance should only be handled in closed systems.

Good sources of information about control methods are as follows:

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to benzidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. The physician should consider whether there exist conditions associated with increased risk, including reduced immunological competence, treatment with steroids or cytotoxic agents, pregnancy, or cigarette smoking. The medical evaluation should concentrate on the function and integrity of the bladder, kidneys, liver, skin, and blood.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is potentially exposed to benzidine. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with bladder, kidney, liver, skin, and blood diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to benzidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benzidine on the bladder, kidneys, liver, skin and blood. OSHA requires periodic examinations annually for workers potentially exposed to benzidine [29 CFR 1910.1010]. Suggested diagnostic tests include urinalysis every month (with particular attention to the presence of occult blood), urine cytology every 6 months, and cystoscopy as indicated. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urine benzidine levels may be useful in biological monitoring to assess exposure. Average urinary benzidine concentrations in workers exposed to benzidine concentrations in the range of 7 to 11 mg/m^3 are reported to be 9 mg benzidine per liter of urine (mg/l). In workers exposed to benzidine concentrations of 140 to 400 mg/m3, urinary benzidine levels reportedly range from 100 to 200 mg/l. As a carcinogen, benzidine or its metabolites should not be detectable in urine or other physiological fluids.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to benzidine may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benzidine is determined by using a glass fiber filter coated with sulfuric acid. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. Immediately after sampling, the filter must be transferred to a vial containing 2 ml of deionized water. Analysis is conducted by gas chromatography using an electron capture detector. The limit of detection for this procedure is 4.1 mg/m^3. This method is described in Method 65 of the *OSHA Analytical Methods Manual* [OSHA 1990].

PERSONAL HYGIENE

If benzidine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water. Get medical help immediately.

Clothing contaminated with benzidine should be removed immediately and should then be discarded.

A worker who handles benzidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where benzidine or a solution containing benzidine is handled, processed, or stored.

STORAGE

Control, handling, processing, and storing of benzidine must be performed in accordance with OSHA's standard for benzidine [29 CFR 1910.1010]. This substance should be isolated in closed systems and should be well ventilated at the points where the system is opened. Containers should be kept closed and be protected from light.

SPILLS

Treat any benzidine spill as an emergency. Preplan for benzidine spills and have a trained team ready to respond in an emergency. Cleanup personnel should be clothed and equipped in a manner that prevents any contact with benzidine.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Benzidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for benzidine is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of benzidine per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benzidine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Benzidine is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U021. This substance has been banned from land disposal and may be treated by incineration. Benzidine also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benzidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with benzidine. All skin and mucous membrane contact with benzidine should be prevented by the wearing of full-body protective clothing and gloves. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benzidine. Contact lenses should not be worn if the potential exists for benzidine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZOYL PEROXIDE

INTRODUCTION

This guideline summarizes pertinent information about benzoyl peroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{14}H_{10}O_4$

- **Structure**

$(C_6H_5CO)_2O_2$

- **Synonyms**

Benzoic acid, benzoperoxide; benzoyl superoxide; diphenylglyoxal peroxide; dibenzoyl peroxide; Acetoxyl; Acnegel; Benzac; Clearasil BP Acne Treatment; Cuticura Acne Cream; Debroxide; Dry and Clear Acne Cream; Epiclear; Fostex; Incidol; Lucidol; Luperco AA; Nayper B; Novadelox; Oxy-5; Oxy Wash; Panoxyl; Persadox; Quinolor Compound; Sulfoxyl; Topex; Vanoxide; Xerac

- **Identifiers**

1. CAS No.: 94-36-0
2. RTECS No.: DM8575000 (for the technical product)
3. DOT UN: 2085 49 (for the technical product)
4. DOT label: Organic Peroxide

- **Appearance and odor**

Benzoyl peroxide is a white crystalline solid that has a faint benzaldehyde odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 242.2
2. Boiling point (at 760 mm Hg): Decomposes explosively at temperatures above 105°C (221°F)
3. Specific gravity (water = 1): 1.33 at 25°C (77°F)
4. Vapor density: Not applicable
5. Melting point: 103° to 105°C (217.4° to 221°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg
7. Solubility: Sparingly soluble in water, alcohol, or vegetable oils; soluble in chloroform, ether, and benzene
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, friction, or impact. Confined storage of dry benzoyl peroxide may lead to decomposition and explosion.
2. Incompatibilities: Benzoyl peroxide is extremely reactive, and fires and explosions may result from contact with strong acids, oxidizing and reducing agents, metals, metal oxides, amines, accelerators, methyl methacrylate, organic matter, carbon tetrachloride and ethylene, dimethylaniline, or lithium aluminum hydride.
3. Hazardous decomposition products: Toxic gases, vapors, and particulates (such as benzoic acid, phenyl benzoate, terphenyls, biphenyls, benzene, carbon monoxide, and carbon dioxide) may be released when benzoyl peroxide decomposes.
4. Special precautions: Benzoyl peroxide is highly reactive and may explode spontaneously; it must be kept wet in a mixture containing at least 1% water.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to benzoyl peroxide.

1. Flash point: 80°C (176°F)
2. Autoignition temperature: 80°C (176°F)
3. Flammable limits in air: Data not available
4. Extinguishant: Use water only; do ***not*** use chemical or carbon dioxide extinguishants.

Fires involving benzoyl peroxide should be fought from an explosionproof location. In advanced or massive fires, the area should be evacuated. Isolate the hazard area and deny access to unnecessary personnel. If fire occurs in the vicinity of containers of benzoyl peroxide, water should be used to keep containers cool. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving benzoyl peroxide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzoyl peroxide is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workshift and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned benzoyl peroxide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of respiratory irritation associated with exposure to benzoyl peroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to benzoyl peroxide can occur through inhalation, ingestion, or contact with the skin or eyes.

- **Summary of toxicology**

1. *Effects on Animals*: Benzoyl peroxide is an irritant of the eyes, mucous membranes, and skin in animals. When instilled into the eyes of rabbits, benzoyl peroxide dust caused irritation [IARC 1985]. A 10% solution of benzoyl peroxide applied to the skin of guinea pigs caused a moderate degree of skin irritation [IARC 1985]. In rats, the 4-hr LC_{50} is estimated to be 700 ppm, and the oral LD_{50} is 7,710 mg/kg [ACGIH 1991a; NIOSH 1991]. During an acute 4-hr exposure to 2,458 ppm (24,300 mg/m^3), rats showed eye tearing and squinting, difficult breathing, excessive salivation, erythema, and motor excitation followed by depression; all animals recovered within the 24- or 48-hr period following termination of exposure [NIOSH 1977]. In a chick embryo assay, embryo toxicity and malformations were induced by benzoyl peroxide [NLM 1991]. Chronic feeding studies in rats showed decreased weight gain in the medium- and high-dose groups and testicular atrophy among males in the high-dose group [IARC 1985].

2. *Effects on Humans*: Benzoyl peroxide is an irritant of the eyes, skin, and mucous membranes in humans. This substance is also a skin sensitizer. Workers exposed to 12.2 mg/m^3 experienced strong irritation of the nose and upper respiratory tract [Proctor et al. 1988]. In prolonged and repeated contact with the skin, benzoyl peroxide has caused dermal irritation and sensitization [IARC 1985].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to benzoyl peroxide can cause moderate to severe irritation of the eyes, nose, and throat, with redness and tearing of the eyes, runny nose, cough, and difficult breathing. In contact with the skin, benzoyl peroxide causes redness and swelling.

2. *Chronic exposure*: Chronic exposure to benzoyl peroxide can cause dermatitis. Some sensitized individuals may also experience whorls, swelling, itching, and redness of the skin.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if benzoyl peroxide is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of benzoyl peroxide may result in worker exposures to this substance:

—Use as an initiator in free radical polymerization

—Use in production of polystyrene and related resins

—Use in auto-repair kits, optical and dental castings, and other molding applications

—Use in vulcanization of natural and synthetic rubbers

—Use in textile manufacture as a burn-out agent for cellulose acetate to produce lace-like appearance in mixed fabrics

—Use in printing pastes

—Use in topical non-prescription medications as a treatment of acne, burns, dermatitis, poisoning, and external wounds, and as an antiseptic and local anesthetic

—Use as a bleaching agent for flour, cheese, fats, oils, and waxes

—Use in the manufacture of special fast-drying inks for printing on plastic surfaces and in the embossing of vinyl flooring

—Use as a fixing agent in light microscopy

The following methods are effective in controlling worker exposures to benzoyl peroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to benzoyl peroxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin and on a history of skin allergies. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to benzoyl peroxide at or below the prescribed exposure limit. The examining licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health licensed medical practitioner. Additional examinations may be necessary if a worker develops symptoms attributable to benzoyl peroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benzoyl peroxide on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for benzoyl peroxide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benzoyl peroxide is determined by using a cellulose ester membrane filter (0.8 micron). Samples are collected at a maximum flow rate of 3 liters/min until a maximum air volume of 400 liters is collected. Immediately after sampling, the sample filters are transferred into a 20-ml scintillation vial and are then sealed and shipped under refrigeration. Upon receipt by the laboratory, the samples are frozen until they are to be analyzed. The sample is then treated with ethyl ether to extract the benzoyl peroxide. Analysis is conducted by high-performance liquid chromatography using ultraviolet light detection. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 5009 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If benzoyl peroxide contacts the skin, workers should remove any contaminated clothing immediately while drenching the affected area with water and then wash with soap and water.

Clothing and shoes contaminated with benzoyl peroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of benzoyl peroxide.

A worker who handles benzoyl peroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where benzoyl peroxide is handled, processed, or stored.

STORAGE

Benzoyl peroxide should be stored in a cool, dry, well-ventilated, fireproof area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Isolated, remote, or detached storage is preferred. The storage area should be equipped with an automatic fire suppression system. To prevent static sparks, all containers and equipment used in shipping, receiving, or transferring operations should be bonded and grounded. Only nonsparking tools may be used with benzoyl peroxide. Any storage system should have an explosion-relief design, and electrical installations and heating facilities should be prohibited in these storage areas. Only the small amount of benzoyl peroxide that is needed for a single work shift should be removed from storage at one time. Containers of benzoyl peroxide should be protected from incompatible chemicals, physical damage, shock, rough handling, friction, sunlight, heat, sparks, and open flame. Because containers that formerly contained benzoyl peroxide may still hold product residues, they should be handled appropriately.

SPILLS

Before benzoyl peroxide is used in the workplace, an emergency plan to handle any contingencies, including spills, should be developed and practiced. In the event of a spill involving benzoyl peroxide, the plan should be implemented. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres using maximum explosionproof ventilation.
5. Cleanup personnel must wear fire-resistant and antistatic protective clothing.
6. Use nonsparking tools for cleanup. Do *not* use cellulosic materials (rags, paper, straw, etc.) to clean up spilled benzoyl peroxide.
7. All benzoyl peroxide spills should be inactivated by adding cold, 10% sodium hydroxide solution to the spilled material in an amount equal to 10 times the weight of the spill. This process takes up to 3 hr to complete.

SPECIAL REQUIREMENTS

The U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Benzoyl peroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of benzoyl peroxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of benzoyl peroxide per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benzoyl peroxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although benzoyl peroxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benzoyl peroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Fire- and static-resistant protective clothing should be worn to prevent skin contact with benzoyl peroxide. Gloves, boots, aprons, and gauntlets are recommended to prevent prolonged or repeated skin contact. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to benzoyl peroxide permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to benzoyl peroxide.

If benzoyl peroxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which benzoyl peroxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benzoyl peroxide. Contact lenses should not be worn if the potential exists for benzoyl peroxide exposure.

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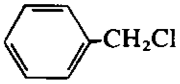
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about benzyl chloride for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_7H_7Cl
- **Structure:**



- **Synonyms:** Alpha-chlorotoluene, chloromethylbenzene
- **Identifiers:** CAS 100-44-7; RTECS XS8925000; DOT 1738, label required: "Poison, Corrosive"
- **Appearance and odor:** Colorless to slightly yellow liquid with a pungent, aromatic, irritating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 126.58
2. Boiling point (at 760 mmHg): 179.4°C (355°F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of benzyl chloride): 4.36
5. Melting point: -39.2°C (-38.6°F)
6. Vapor pressure at 22°C (71.6°F): 1 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.05
8. Evaporation rate (butyl acetate = 1): 0.11
9. Saturation concentration in air (approximate) at 22°C (71.6°F): 0.13% (1300 ppm)

- **Reactivity**

1. Incompatibilities: Contact with active metals such as copper, aluminum, magnesium, iron, zinc, and tin may cause the liberation of heat and hydrogen chloride. Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving benzyl chloride.
3. Caution: Benzyl chloride will attack some forms of plastic, rubber, and coatings.

- **Flammability**

1. Flash point: 67°C (153°F) (closed cup)
2. Autoignition temperature: 585°C (1085°F)
3. Flammable limits in air, % by volume: Lower, 1.1; Upper, Not available
4. Extinguishant: Dry chemical, foam, carbon dioxide, or water spray
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.04 ppm
2. Eye irritation level: 16 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor and irritant effects, benzyl chloride can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzyl chloride is 1 part of benzyl chloride per million parts of air (ppm) [5 milligrams of benzyl chloride per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 1 ppm (5 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 1 ppm (5 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for benzyl chloride

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	1	5
NIOSH REL Ceiling (15 min)	1	5
ACGIH TLV® TWA	1	5

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Benzyl chloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute subcutaneous injection of benzyl chloride in rats caused labored breathing, bloody diarrhea, lung edema with bleeding, and liver damage. Acute inhalation of benzyl chloride by cats caused irregular respiration, inactivity, marked unresponsiveness, and death due to hemorrhage in the lungs; the surviving cats later developed clouded corneas, conjunctivitis, and severe pneumonia. Chronic subcutaneous injection of benzyl chloride in rats produced injection-site skin cancer and lung metastases. Oral administration of benzyl chloride to rats during pregnancy caused increased embryolethality and retarded postnatal development. NIOSH will continue to monitor the research regarding benzyl chloride to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.
2. *Effects on humans:* Long-term exposure of workers to benzyl chloride has caused increased incidences of respiratory illness and dermatitis, abnormal liver function and serum protein levels, and decreased white blood cell counts. An increased incidence of lung cancer has been reported for workers potentially exposed to benzyl and benzoyl chlorides.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to benzyl chloride can cause weakness, persistent headache, irritability, sweating, tremors, and loss of sleep and appetite. Skin sensitization, intense inflammation of the mucous membranes, and corneal damage can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of revelant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to benzyl chloride, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, liver, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzyl chloride at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to benzyl chloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, liver, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according ot standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to benzyl chloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzyl chloride. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting benzyl chloride vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure benzyl chloride may also be used if available. A detailed sampling and analytical method for benzyl chloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1003).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with benzyl chloride.

Workers should be provided with and required to use splash-proof safety goggles where benzyl chloride may come in contact with the eyes.

SANITATION

Clothing which is contaminated with benzyl chloride should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of benzyl chloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzyl cloride's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with benzyl chloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle benzyl chloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzyl chloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for benzyl chloride

Operations	Controls
During use in the production of benzyl compounds	Process enclosure, local exhaust ventilation, personal protective equipment
During use in polymerization as a reactant catalyst, accelerator, and promoter; during use in rubber adhesives and TV tubes	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a raw material for pickling inhibitors, gasoline gum inhibitors, and synthetic tanning agents; during use in the processing of starch and the preparation of textile fibers	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assitance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to benzyl chloride, an eye-wash fountain should be provided within the immediate work area for emergency use. If benzyl chloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to benzyl chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzyl chloride gets on the skin, wash it immediately with soap and water. If benzyl chloride penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If benzyl chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing benzyl chloride, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from benzyl chloride vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing benzyl chloride may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Benzyl chloride should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing benzyl chloride may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for benzyl chloride

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 10 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any powered air-purifying respirator with organic vapor and acid gas cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection) Any chemical cartridge respirator with organic vapor and acid gas cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection) Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor and acid gas canister Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Planned or emergency entry into environments containing unknown concentrations or levels above 10 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor and acid gas canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (5 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BERYLLIUM AND ITS COMPOUNDS

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about beryllium and its compounds for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** Be
- **Synonyms:** Synonyms vary depending upon specific compound
- **Identifiers:** CAS 7440-41-7; RTECS DS1750000; DOT 1567, label required: "Poison, Flammable Solid"
- **Appearance:** Silvery gray metal

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 9.01
2. Boiling point (at 760 mmHg): 2,970°C (5,378°F)
3. Specific gravity (water = 1): 1.85
4. Melting point: 1,283°C (2,341°F)
5. Insoluble in water

- **Reactivity**

1. Incompatibilities: Acids, alkalies, chlorinated hydrocarbons, and oxidizable agents
2. Hazardous decomposition products: Beryllium reacts with strong acids to evolve hydrogen.

- **Flammability**

1. Extinguishant: Sand, soda ash, or commercial metal fire extinguishant powder may be used. Do not use water or carbon dioxide.
2. Flammability Rating 1 (NFPA)
3. Caution: Powdered beryllium is flammable in air. Hazard increases as fineness of powder increases.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for beryllium and its compounds is 2 micrograms of beryllium per cubic meter of air ($\mu g/m^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 5 $\mu g/m^3$; and the maximum peak concentration above the acceptable ceiling concentration (maximum duration of 30 minutes) is 25 $\mu g/m^3$. The National Institute for Occupational Safety and Health (NIOSH) recommends that beryllium be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible level. The NIOSH recommended exposure limit (REL) is that occupational exposure to beryllium be controlled so that no worker will be exposed in excess of 0.5 $\mu g/m^3$. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated beryllium as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 2 $\mu g/m^3$ as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for beryllium

	Exposure limits $\mu g/m^3$
OSHA PEL TWA	2
Acceptable ceiling	5
Maximum peak above ceiling (30 min)	25
NIOSH REL (Ca)*	
No exposure in excess of	0.5
ACGIH TLV® TWA (A2)†	2

* (Ca): NIOSH recommends treating as a potential human carcinogen.

† (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Beryllium may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

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National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• Summary of toxicology

1. *Effects on animals:* Chronic inhalation or intratracheal injection of beryllium metal or its compounds produced lung cancer in rats. Single intrabronchial implantations of beryllium oxide or chronic inhalation of beryllium sulfate produced lung cancer in monkeys. In rabbits, intraosseous administration of beryllium metal or its compounds produced bone cancer.
2. *Effects on humans:* Acute or chronic inhalation of beryllium has caused rhinitis (inflammation of the mucous membranes of the nose), tracheobronchitis (inflammation of the trachea and bronchi), pneumonitis (inflammation of the lungs), and death due to pulmonary edema or heart failure. Chronic inhalation of beryllium has been associated with kidney stones; enlargement of the liver, spleen, and heart; multiple granulomas of the lung, spleen, liver, and lymph nodes; and an increased incidence of lung cancer.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to beryllium can cause pain below the sternum, weight loss, nonproductive cough, shortness of breath, and irritation of the eyes, respiratory system, and skin.
2. *Long-term (chronic):* Exposure to beryllium can cause cough, pain in the joints, general weakness, weight loss, clubbing of fingers, shortness of breath, cyanosis, and allergic contact dermatitis. Accidental implantation of beryllium metal or crystals into the skin can cause tissue necrosis and ulceration.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to beryllium, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, spleen, and cardiovascular and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to beryllium at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and significant breathing impairment due to preexisting chronic lung disease. Skin patch testing with soluble beryllium compounds is *not* recommended because of the risk of sensitization.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to beryllium. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, kidneys, spleen, and cardiovascular and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires, tests of lung function, and chest X-rays. In the event of the occurrence of a chronic respiratory disease, diagnostic tests such as the lymphocyte transformation test may be useful in determining the role of beryllium sensitization.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to beryllium may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Chronic beryllium disease of the lungs.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting beryllium with cellulose membrane filters followed by digestion with acid and analysis by flameless atomic absorption with a graphite furnace. A detailed sampling and analytical method for beryllium may be found in the *NIOSH Manual of Analytical Methods* (method number 7102).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with beryllium.

SANITATION

Clothing which is contaminated with beryllium should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of beryllium from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beryllium's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with beryllium should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle beryllium should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to beryllium may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for beryllium

Operations	Controls
During use in the manufacture of electrical components and ceramics	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the production of beryllium metal from ore	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the production of alloy	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to beryllium, an eye-wash fountain should be provided within the immediate work area for emergency use.

If beryllium gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to beryllium, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If beryllium gets on the skin, wash it immediately with soap and water. If beryllium penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If beryllium is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities of liquids containing beryllium or beryllium compounds, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing beryllium or beryllium compounds may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Beryllium dust may be collected by vacuuming with an appropriate high-efficiency filtration system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for beryllium

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BISMUTH TELLURIDE DOPED WITH SELENIUM SULFIDE

INTRODUCTION

This guideline summarizes pertinent information about doped bismuth telluride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Bi_2Te_3 doped with Bi_2Se_3, SnTe, and Te

- **Synonyms**

Doped bismuth sesquitelluride, doped bismuth tritelluride, doped dibismuth tritelluride, doped tellurobismuthite

- **Identifiers**

1. CAS No.: 1304-82-1
2. RTECS No.: EB3110000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Bismuth telluride doped with selenium is a nonflammable, gray, crystalline solid that has been enhanced (or doped) with a small amount of a selenium compound; doping confers on the semiconductor the charge characteristics of the doping agent, which alters the conductivity of the semiconductor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 800.76
2. Boiling point: Data not available
3. Specific gravity (water = 1): 7.7 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 573°C (1,063.4°F)
6. Vapor pressure: Not applicable
7. Solubility: Insoluble in water; decomposes in nitric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: A violent reaction may result from contact of doped bismuth telluride with strong oxidizers (such as bromine, fluorine, or chlorine), and a toxic gas may evolve from contact with moisture.
3. Hazardous decomposition products: Toxic materials (such as tellurium) may be released in a fire involving doped bismuth telluride.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to doped bismuth telluride; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant suitable for the materials involved in the surrounding fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving doped bismuth telluride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bismuth telluride doped with selenium sulfide is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established an 8-hr TWA of 5 mg/m^3 as the recommended exposure limit (REL) for bismuth telluride doped with selenium sulfide [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bismuth telluride doped with selenium sulfide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of respiratory effects associated with exposure to doped bismuth telluride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to doped bismuth telluride can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals*: Selenium-doped bismuth telluride causes reversible, nonfibrotic lesions in the lungs of exposed experimental animals [Clayton and Clayton 1981]. Dogs, rabbits, and rats were exposed to 15 mg/m^3 of a dust (average particle size 1.04 microns) containing a mixture of doped bismuth telluride and stannous telluride for 6 hr/day, 5 days/week for 1 year. The dogs and rabbits developed small granulomatous lesions in the lungs, and the rats developed epithelialization of the alveolar walls [ACGIH 1991a; Clayton and Clayton 1981]. Fibrotic changes did not occur in any species; in dogs examined 4 months after the cessation of exposure, these lesions had regressed, indicating reversibility [ACGIH 1991a; Clayton and Clayton 1981].

2. *Effects on Humans*: No adverse effects of exposure to doped bismuth telluride have been noted in humans except for the development of "tellurium breath" (breath that smells like garlic) [Clayton and Clayton 1981]. Based on effects seen in animals, overexposure to the dust of doped bismuth telluride is likely to cause reversible pulmonary changes in humans [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to doped bismuth telluride can cause garlic breath and local irritation of the eyes and skin.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to doped bismuth telluride have been reported in humans.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: If a large amount of doped bismuth telluride is ingested take the following steps:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

Use of doped bismuth telluride as a semiconductor may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to doped bismuth telluride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to doped bismuth telluride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to doped bismuth telluride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

• Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to doped bismuth telluride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of doped bismuth telluride on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for doped bismuth telluride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and the selected physiologic or laboratory tests conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne selenium-doped bismuth telluride (measured as bismuth) is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989] and in the OSHA Computerized Information System [OSHA 1990].

PERSONAL HYGIENE

If the dust of doped bismuth telluride collects on the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with doped bismuth telluride should be removed.

A worker who handles doped bismuth telluride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where doped bismuth telluride is handled, processed, or stored.

STORAGE

Doped bismuth telluride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of doped bismuth telluride should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained doped bismuth telluride may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving doped bismuth telluride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Doped bismuth telluride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of doped bismuth telluride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of doped bismuth telluride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although doped bismuth telluride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of doped bismuth telluride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with doped bismuth telluride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to doped bismuth telluride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to doped bismuth telluride.

If doped bismuth telluride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which doped bismuth telluride might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with doped bismuth telluride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BISMUTH TELLURIDE, UNDOPED

INTRODUCTION

This guideline summarizes pertinent information about undoped bismuth telluride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Bi_2Te_3

- **Synonyms**

Bismuth sesquitelluride, bismuth tritelluride, dibismuth tritelluride, tellurobismuthite

- **Identifiers**

1. CAS No.: 1304-82-1
2. RTECS No.: EB3110000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Undoped bismuth telluride is a gray, crystalline solid that is not flammable.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 800.76
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 7.7 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 573°C (1,063.4°F)
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Insoluble in water; decomposes in nitric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: A violent reaction may result from contact of undoped bismuth telluride with strong oxidizers (such as bromine, fluorine, or chlorine), and a toxic gas may evolve from contact with moisture.
3. Hazardous decomposition products: Toxic materials (such as tellurium) may be released in a fire involving undoped bismuth telluride.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to undoped bismuth telluride; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving undoped bismuth telluride.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for undoped bismuth telluride is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for undoped bismuth telluride of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned undoped bismuth telluride a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of physical irritation associated with exposure to undoped bismuth telluride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to undoped bismuth telluride can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals*: Dogs, rabbits, and rats exposed to undoped bismuth telluride dust (average particle size 0.4 micron) at 15 mg/m^3 for 6 hr/day, 5 days/week for 11 months showed no adverse responses other than accumulation of this substance in the lungs [Cralley and Cralley 1985].

2. *Effects on Humans*: In humans, exposure to the dust of undoped bismuth telluride causes physical irritation of the eyes, nose, and throat [NJDH 1985]. Long-term exposure causes accumulation of dust in the lungs; this dust is radiographically visible [NJDH 1985].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to undoped bismuth telluride can cause local irritation of the eyes and skin.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to undoped bismuth telluride have been reported.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if undoped bismuth telluride is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of undoped bismuth telluride may result in worker exposures:

—Use for thermoelectric cooling

—Use as a semiconductor

The following methods are effective in controlling worker exposures to undoped bismuth telluride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to undoped bismuth telluride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to undoped bismuth telluride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to undoped bismuth telluride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of undoped bismuth telluride on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for undoped bismuth telluride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne undoped bismuth telluride (measured as bismuth) is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989] and in the OSHA Computerized Information System [OSHA 1990].

PERSONAL HYGIENE

If the dust of undoped bismuth telluride collects on the skin in excessive amounts, workers should wash the affected areas with soap and water.

Clothing contaminated with the dust of undoped bismuth telluride should be removed.

A worker who handles undoped bismuth telluride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where undoped bismuth telluride is handled, processed, or stored.

STORAGE

Undoped bismuth telluride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [40 CFR 1910.1200]. Containers of undoped bismuth telluride should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained undoped bismuth telluride may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving undoped bismuth telluride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area for reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Undoped bismuth telluride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of undoped bismuth telluride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of undoped bismuth telluride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although undoped bismuth telluride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of undoped bismuth telluride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with undoped bismuth telluride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to undoped bismuth telluride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to undoped bismuth telluride.

If undoped bismuth telluride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which undoped bismuth telluride might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with undoped bismuth telluride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BORON OXIDE

INTRODUCTION

This guideline summarizes pertinent information about boron oxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

B_2O_3

- **Synonyms**

Anhydrous boric acid, boric anhydride, boric oxide, boron sesquioxide, boron trioxide, diboron trioxide, fused boric acid

- **Identifiers**

1. CAS No.: 1303-86-2
2. RTECS No.: ED7900000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Boron oxide is a noncombustible, odorless, colorless or white, brittle substance that occurs as hygroscopic granules or in flake or powder form.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 69.6
2. Boiling point (at 760 mm Hg): 1,842°C (3,380°F)
3. Specific gravity: 2.5 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 450°C (842°F)
6. Vapor pressure at 20°C (68°F): Approximately 0 mm Hg
7. Solubility: Soluble in ethanol, glycerol, and hot water; slightly soluble in cold water
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Boron oxide reacts slowly with water to form boric acid.
2. Incompatibilities: Fires and explosions may result from contact of boron oxide with bromine pentafluoride or calcium oxide.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

This substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron oxide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving boron oxide.

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EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for boron oxide is 10 mg/m^3 (total dust) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for boron oxide of 10 mg/m^3 as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned boron oxide a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye and upper respiratory tract irritation associated with exposure to boron oxide.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to boron oxide can occur through inhalation, ingestion, or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Boron oxide is an irritant of the skin and mucous membranes in animals. The oral LD_{50} in mice is 3,163 mg/kg [NIOSH 1991]. Application of boron oxide dust to the shaved skin of rabbits caused redness that persisted for several days [Wilding et al. 1959]. When instilled into the eyes of rabbits, the dust caused conjunctivitis [Wilding et al. 1959]. Rats exhibited mild nasal irritation when exposed to a boron oxide aerosol at 470 mg/m^3 for 6 hr/day, 5 days/week for 10 weeks [NLM 1991; ACGIH 1991a]. Young rats intubated with a 10% boron oxide slurry for 3 weeks showed no adverse effects [ACGIH 1991a].

2. *Effects on Humans*: Exposure to boron oxide causes irritation of the eyes and respiratory tract; dryness of the mouth, nose, and throat; sore throat; and a productive cough [Garabrant et al. 1984]. A group of 113 workers exposed to the dust of boron oxide and boric acid at mean concentrations of 4.1 mg/m^3 (range 1.2 to 8.5 mg/m^3; exposures occasionally in excess of 10 mg/m^3) exhibited statistically significant increases in eye, nose, and upper respiratory tract symptoms [Garabrant et al. 1984].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to boron oxide can cause pain and redness of the eyes, tearing, irritation of the nasal membranes, sore throat, and cough.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to boron oxide have been reported.

• Emergency procedures

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if boron oxide is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve boron oxide and may result in worker exposures to this substance:

—Preparation of fluxes for enamels and glazes

—Laboratory analysis of silicates

—Manufacture of glass for heat-resistance

—Use of boron oxide in blowpipe analysis

—Application as a herbicide

—Production of surface coatings and use of boron oxide in the electronics industry

—Production of boron, boron master alloys, borides, metal borates, and boron carbide, nitrides, and halides

—Use of boron oxide as an additive to provide fire-resistance to enamels, paints, and insulation

—Use of boron oxide as an additive for glass fibers

The following methods are effective in controlling worker exposures to boron oxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to boron oxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to boron oxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye or skin diseases.

• Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to boron oxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of boron oxide on the eyes or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Serum borate concentrations are qualitative indicators of exposure to borate compounds (including boron oxide), but these levels cannot be correlated with airborne concentrations of borates. Therefore, no biological monitoring test acceptable for routine use has yet been developed for boron oxide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne boron oxide is determined by using tared, low-ash polyvinyl chloride filters (5-micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. This is a gravimetric field test method based on the total weight collected and does not need to be submitted to the laboratory for analysis. This method is described in the section on filter weighing procedures in the *OSHA Chemical Information Manual* [OSHA 1987]. Additional information can be found in Method 0500 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If boron oxide contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min and then wash with soap and water.

Clothing contaminated with boron oxide should be removed promptly.

A worker who handles boron oxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where boron oxide or a solution containing boron oxide is handled, processed, or stored.

STORAGE

Boron oxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of boron oxide should be protected from physical damage, kept dry, and stored separately from bromine pentafluoride or calcium oxide, heat, sparks, and open flame. Because containers that formerly contained boron oxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving boron oxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill.

1. Scoop up spilled material and place the material in a covered container for later reclamation or disposal.

2. Avoid generating dust during cleanup by using a vacuum or a wet method.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Boron oxide is not subject to EPA emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of boron oxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form

(Form R) to EPA reporting the amount of boron oxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although boron oxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of boron oxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent repeated skin contact with boron oxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to boron oxide permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to boron oxide.

If boron oxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which boron oxide might contact the eyes (e.g., through dust particles or splashes of boric acid). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with boron oxide. Contact lenses should not be worn if the potential exists for boron oxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BORON TRIBROMIDE

INTRODUCTION

This guideline summarizes pertinent information about boron tribromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

BBr_3

- **Synonyms**

Boron bromide; tribromoborane, trona

- **Identifiers**

1. CAS No.: 10294-33-4
2. RTECS No.: ED7400000
3. DOT UN: 2692 59
4. DOT label: Corrosive

- **Appearance and odor**

Boron tribromide is a colorless, fuming, nonflammable, volatile liquid with a sharp, irritating odor. No quantitative data are available on the odor threshold for boron tribromide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 250.6
2. Boiling point (760 mm Hg): 90°C (194°F)
3. Specific gravity (water - 1): 2.7 at 0°C (32°F)
4. Vapor density (air - 1 at boiling point of boron tribromide): 8.6
5. Melting point: -46°C (-51°F)
6. Vapor pressure at 33.5°C (92.3°F), 100 mm Hg; at 14°C (57.1°F), 40 mm Hg
7. Solubility: Decomposes in water or alcohol; soluble in carbon tetrachloride and sulfur dioxide
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Fire and explosions may result from contact of boron tribromide with water, steam, potassium, sodium, or alcohol.
3. Hazardous decomposition products: Toxic gases and particulates (such as hydrogen bromide, oxides of boron, and oxides of bromine) may be released in a fire involving boron tribromide.
4. Special precautions: Boron tribromide attacks metals, wood, rubber, and Bakelite® but does not attack Teflon® or stainless steel.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to boron tribromide; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron tribromide should be fought upwind and from the maximum distance possible. Isolate the hazard

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Containers of boron tribromide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving boron tribromide. Firefighters' protective clothing may not provide protection against permeation by boron tribromide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for boron tribromide is 1 ppm (10 mg/m^3) as a ceiling limit. A worker's exposure to boron tribromide shall at no time exceed this limit [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (10 mg/m^3) as a ceiling limit [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned boron tribromide a threshold limit value (TLV) of 1 ppm (10 mg/m^3) as a ceiling limit that should not be exceeded during any part of the working exposure [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation associated with exposure to boron tribromide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to boron tribromide can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: No acute toxicity data specific to boron tribromide is available. However, the toxicity and action of boron tribromide is similar to that of boron trichloride, which causes marked swelling and burns in contact with the eyes, skin, or mucous membranes; hemorrhages of the lungs, kidneys, and intestines in some animals acutely exposed to lethal concentrations; and death in all mice and rats exposed to 20 ppm for 7 hr [Clayton and Clayton 1981]. The LC_{50} for a 1-hr exposure to hydrogen bromide, a hydrolysis product of boron tribromide, is 814 ppm in the mouse and 2,858 ppm in the rat [Sax and Lewis 1989].

2. *Effects on Humans*: Boron tribromide is an irritant that is strongly corrosive because of its rapid hydrolysis to boric acid and hydrogen bromide [ACGIH 1991a; Clayton and Clayton 1981]. Acute exposure to boron tribromide causes marked irritation of the eyes, nose, throat, and skin, and contact of the eyes or skin with boron tribromide leads to burns [NJDH 1985]. Pulmonary edema, which is potentially life threatening, may result from acute respiratory exposure to boron tribromide [NJDH 1985]. A chemist who splashed boron tribromide into his eyes experienced no pain at the time but subsequently developed permanent corneal injury, including corneal opacification, in the most severely exposed eye; the other eye gradually returned to normal [Grant 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to boron tribromide can cause redness, swelling, and tearing of the eyes; runny nose; coughing; and shortness of breath. Contact of this substance with the skin or eyes may lead to burns of the affected tissues.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to boron tribromide have been reported.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of boron tribromide! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of boron tribromide are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if boron tribromide or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve boron tribromide and may result in worker exposures to this substance:

—Use of boron tribromide as a catalyst in organic synthesis

—Production of diborane and ultra-high-purity boron

—Manufacture of semiconductors

The following methods are effective in controlling worker exposures to boron tribromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to boron tribromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to boron tribromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to boron tribromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of boron tribromide on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for boron tribromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne boron tribromide is determined by using a midget fritted-glass bubbler containing 10 ml of 0.003M $NaHCO_3$/0.0024 M Na_2CO_3. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 5 liters is collected. Analysis is conducted by ion chromatography. The limit of detection for this procedure is 0.01 mg/m^3. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If boron tribromide contacts the skin, workers should immediately flood the affected areas with water and then wash with soap and water.

Clothing and shoes contaminated with boron tribromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of boron tribromide, particularly its potential to cause skin burns.

A worker who handles boron tribromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where boron tribromide or a solution containing boron tribromide is handled, processed, or stored.

STORAGE

Boron tribromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of boron tribromide should be protected from physical damage and should be stored away from water, steam, potassium, sodium, alcohol, heat, sparks, and open flame. Because containers that formerly contained boron tribromide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving boron tribromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.

6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the boron tribromide for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Boron tribromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of boron tribromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of boron tribromide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although boron tribromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of boron tribromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with boron tribromide. Full-body protection and gloves are recommended to prevent skin contact with this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Chlorinated polyethylene has demonstrated fair to good protection against permeation by boron tribromide.

If boron tribromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which boron tribromide might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with boron tribromide. Contact lenses should not be worn if the potential exists for boron tribromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BORON TRIFLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about boron trifluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

BF_3

- **Synonyms**

Trifluoroboron, boron fluoride, trifluoroborane

- **Identifiers**

1. CAS No.: 7637-07-2
2. RTECS No.: ED2275000
3. DOT UN: 1008 15
4. DOT label: Nonflammable Gas and Poison

- **Appearance and odor**

Boron trifluoride is a nonflammable, colorless gas that fumes in moist air and has a pungent, irritating odor. The odor threshold is reported to range from 1 to 1.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 67.8
2. Boiling point (at 760 mm Hg): -100°C (-148°F)
3. Specific gravity (water = 1): 2.99 at 20°C (68°F)
4. Relative density (air = 1 at boiling point of boron trifluoride): 2.3
5. Melting point: -127.1°C (-196.8°F)
6. Vapor pressure at 20°C (68°F): Greater than 1 mm Hg
7. Solubility: Soluble in water and in most saturated and halogenated hydrocarbons and aromatic compounds; very soluble in concentrated acids and organic solvents
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Boron trifluoride hydrolyzes in moist air to boric acid, hydrogen fluoride, and fluoboric acid. It also decomposes in hot water to form boric acid and fluoboric acid. This substance also decomposes when heated.
2. Incompatibilities: Fires and explosions may result from contact of boron trifluoride with alkali metals, alkaline earth metals (except magnesium), alkyl nitrate, or calcium oxide. Boron trifluoride incandesces when heated with alkali metals or alkaline earth metals (except magnesium).
3. Hazardous decomposition products: Toxic gases and vapors (such as fluorine and fluorine compounds) may be released when boron trifluoride is heated to decomposition.
4. Special precautions: Boron trifluoride corrodes most metals in the presence of moisture.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to boron trifluoride; this substance is not flammable and will not support combustion.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

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Fires involving boron trifluoride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of boron trifluoride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do not get water inside containers. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Firefighters should wear a full set of protective clothing, including a self-contained breathing apparatus, when fighting fires involving boron trifluoride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for boron trifluoride is 1 ppm (3 mg/m^3) of air as a ceiling limit. A worker's exposure to boron trifluoride shall at no time exceed this ceiling limit [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (3 mg/m^3) as a ceiling limit [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned boron trifluoride a ceiling limit of 1 ppm (2.8 mg/m^3), which should not be exceeded during any part of the working day [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of severe pulmonary irritation associated with exposure to boron trifluoride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to boron trifluoride can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Boron trifluoride is potentially a corrosive poisonous gas that can cause burns to the nasal and respiratory passages, eyes, and skin. It can also be dermally absorbed. Acute exposure of guinea pigs to 100 ppm resulted in the death of all animals. The 1-hr and 4-hr LC$_{50}$s for rats are 387 (320-467) and 393 ppm, respectively. Before the deaths of these animals, they exhibited respiratory irritation, pneumonia, kidney damage, retarded growth, and severe progressive dental fluorosis [NLM 1991]. In six studies, subchronic exposure of multiple species spanned 0.67 to 100 ppm for 0.5 to 6 months [NLM 1991]. Irritation was noted at all reported levels. Serum chemistry changes (dysproteinemia, decreased globulinemia and cholinesterase), nervous lability, decreased body weight, and pneumonitis occurred at 1 to 4 ppm over a 3 to 6 month exposure period. Rales, renal tubular necrosis, and death occurred at 6 ppm following 3 to 6 months of exposure. Progressive pulmonary involvement (difficult breathing, pneumonitis, emphysema, and alveolar collapse) and death from respiratory failure were noted during months 3 to 6 at 12.8 ppm. Increased lung and liver weights were noted in animals exposed to 22 or 60 ppm for 2 weeks. A 1-month exposure of six species to 100 ppm caused lung and kidney damage and the death of all animals [NLM 1991].

2. *Effects on Humans*: Boron trifluoride is a severe irritant of the nasal passages, lungs, skin, and eyes in humans, producing burns similar to those caused by hydrofluoric acid. Because this substance forms acids when it comes into contact with moisture, the eyes and skin can be severely burned if exposed to boron trifluoride. Exposure at 50 ppm for 30 to 60 min is believed to be lethal to humans [Braker and Mossman 1980]. Eight of 13 workers exposed for 1 to 27 years to boron trifluoride concentrations ranging from an estimated 0.1 to 1.8 ppm showed decreased pulmonary function (forced ventilatory capacity and expiratory volume) on clinical examination, although their chest X-rays were normal [Clayton and Clayton 1981]. A group of 78 workers exposed for 10 to 15 years to boron trifluoride at unspecified concentrations (estimated occasionally to be as high as 32 ppm) developed nosebleeds and dryness of the nasal mucosa, bleeding gums, dry and scaly skin, and joint pain. Concurrent exposures to ethylene and isobutylene were also reported [Parmeggiani 1983; Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Severe ambient exposure to boron trifloride can cause severe irritation or burns of the eyes, eyelids, and skin, inflammation and congestion of the lungs, cardiovascular collapse, respiratory failure, and death. Direct tissue contact with the gas can cause frostbite. Inhalation can induce severe salivation, nausea, gastritis, gastroenteritis, abdominal pain, retching, and prolonged vomiting with hematemesis, watery or tarry diarrhea, dehydration, shock, palor, cyanosis, coldness, rapid weak

pulse, rapid shallow breathing, drowsiness, hyporeflexia or convulsions, dilated pupils, coma, and death. Survivors may develop pyloric stenosis, hepatic cirrhosis, and renal damage.

2. *Chronic exposure*: Chronic exposure to boron trifluoride can cause nosebleeds and dryness of the nasal mucosa, bleeding gums, dry and scaly skin, joint pain, osteosclerosis, increased bone density and brittleness, mottled tooth enamel, weight loss, anemia, weakness, and decreased pulmonary function.

- **Emergency procedures**

WARNING

Exposed victims may die.
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***. In addition, tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: If frostbite occurs, seek medical attention ***immediately***. In addition, severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If boron trifluoride is inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of boron trifluoride may result in worker exposures to this substance:

—Use as a Lewis acid catalyst for alkylation of aromatic compounds and in the polymerization of phenolic and epoxy resins

—Use in nuclear technology for separation of boron isotopes, as a filling gas for neutron counters, in the production of neutron-absorbing salts for molten-salt breeder reactors, and in ionization chambers to detect weak neutrons

—Use as a fumigant

—Use in gas brazing and in the production of diborane and other boron-containing compounds

—Use in the electronics industry to treat separators for high-temperature cells, to prepare high-breakdown voltage varistors, and to enhance the surface conductivity of perylene

—Use in the magnesium industry during casting and heat-treating operations as a fire retardant and antioxidant

The following methods are effective in controlling worker exposures to boron trifluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to boron trifluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, kidneys, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to boron trifluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system, kidney, or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to boron trifluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of boron trifluoride on the respiratory system, kidneys, and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary fluoride is a nonspecific indicator of exposure to a fluoride compound. Maintaining preshift and postshift urinary fluoride concentrations below 4 and 7 mg/g creatinine, respectively, appears to protect against the development of bony fluorosis.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to boron trifluoride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

Neither NIOSH nor OSHA has a recommended method for sampling boron trifluoride in the workplace. However, the following secondary analytical method, which has not been validated, is available. A worker's exposure to airborne boron trifluoride is determined by using a midget fritted-glass bubbler containing 10 ml of 0.1M ammonium fluoride. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 480 liters is collected. A stock standard is made by dissolving 0.125 g of potassium tetrafluoroborate in 100 ml of 0.1M ammonium fluoride. Working standards are then made by making serial dilutions of the stock standard in 0.1M ammonium fluoride to the appropriate ranges. Analysis is done using the fluoborate specific-ion electrode and a double junction reference electrode. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If boron trifluoride contacts the skin, the victim should immediately and thoroughly wash the affected areas with soap and water. Medical attention should be obtained immediately.

Clothing contaminated with boron trifluoride should be removed immediately. In case of massive exposure, the contaminated clothing should be removed under a drenching safety shower and medical attention should be obtained immediately.

A worker who is exposed to boron trifluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where boron trifluoride is present.

STORAGE

Boron trifluoride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage in a non-combustible structure is preferred. Cylinders should be stored and handled in accordance with OSHA's compressed gases standard [29 CFR 1910.101]. Containers of boron trifluoride should be protected from physical damage and should be stored separately from alkali metals, alkaline earth metals (except magnesium), alkyl nitrates, calcium oxide, heat, sparks, and open flame. Because containers that formerly contained boron trifluoride may still hold product residues, they should be handled appropriately.

LEAKS

Before boron trifluoride is used in the workplace, emergency procedures should be established and made known to all affected personnel. In the event of a leak involving boron trifluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Evacuate the leak area for at least 50 ft in all directions.
2. Notify safety personnel.
3. Stop the leak or remove the leaking cylinder if this can be done safely.
4. Do not get water inside cylinders containing boron trifluoride.
5. Flush the leak area with enough water to flood it.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 500 lb or more of boron trifluoride onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for boron trifluoride is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of boron trifluoride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although boron trifluoride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of boron trifluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with boron trifluoride. Gloves, aprons, coveralls, long sleeves, and other protective equipment are recommended as necessary for workers exposed to boron trifluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to boron trifluoride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to boron trifluoride.

If boron trifluoride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which boron trifluoride gas might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with boron trifluoride. Contact lenses should not be worn if the potential exists for boron trifluoride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMACIL

INTRODUCTION

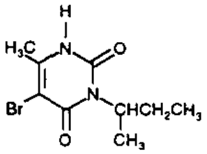
This guideline summarizes pertinent information about bromacil for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{13}BrN_2O_2$

- **Structure**



- **Synonyms**

Borea; bromazil; 5-bromo-6-methyl-3-(1-methyl propyl)-2,4(1*H*,3*H*)-pyrimidinedione; 5-bromo-6-methyl-3-(1-methylpropyl)-uracil; 5-bromo-3-sec-butyl-6-methyl-uracil; Cynogan; Eerex Granular Weed Killer; Eerex Water Soluble Concentrate Weed Killer; Herbicide 976; Hyvar; Hyvarex; isocil; Krovar II; Nalkil; Uragan; Uragon; Urox B.

- **Identifiers**

1. CAS No.: 314-40-9
2. RTECS No.: YQ9100000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Bromacil is an nonflammable, odorless, colorless-to-white, crystalline substance. It is commercially available as a wettable powder, liquid formulation, and mixture with various other agricultural chemicals. Bromacil-containing mixtures and liquid formulations may be combustible.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 261.11
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 1.55 at 25°C (77°F)
4. Vapor density: Data not available
5. Melting point: 157.5° to 160°C (313.7° to 320°F): slowly sublimes
6. Vapor pressure at 100°C (212°F): 0.0008 mm Hg
7. Solubility: Slightly soluble in water; moderately soluble in xylene, strong aqueous bases, acetone, acetonitrile, and ethanol; sparingly soluble in hydrocarbons.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame.
2. Incompatibilities: Decomposes slowly upon contact with strong acids.
3. Hazardous decomposition products: Toxic gases (such as bromine and oxides of nitrogen) may be released in a fire involving bromacil.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to bromacil. It may burn in its solid form,

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but it does not ignite easily. Liquid formulations or mixtures containing bromacil may be combustible.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromacil.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromacil is 1 ppm (10 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (10 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromacil a threshold limit value (TLV) of 1 ppm (10 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of thyroid-damaging and irritant effects associated with exposure to bromacil.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to bromacil can occur through inhalation or ingestion.

- **Summary of toxicology**

1. *Effects on animals*: Bromacil is an irritant of the eyes and upper respiratory tract in experimental animals; this substance has also been shown to have endocrine and reproductive effects in rodents. When instilled into the eyes of rabbits, this substance caused reversible conjunctival irritation but no corneal damage [Grant 1986]. When applied to the skin of guinea pigs, bromacil caused mild to moderate irritation but was not a skin sensitizer [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is greater than 5 g/kg [NIOSH 1991]. The oral LD_{50} in rats is 641 mg/kg and does not induce signs or symptoms. Acute administration of 1,100 mg/kg to dogs induced salivation, vomiting, muscular weakness, excitability, diarrhea, and mydriasis. Chickens and cattle developed weight loss and abnormal gait following an oral dose of 250 mg/kg. Toxic symptoms in poisoned animals include anorexia, depression, tympanites, and increased respiratory rates. One dog survived a 5 g/kg dose [NLM 1992]. Male rats were given bromacil 5 days/week for 2 weeks at oral doses of 650, 1,035, or 1,500 mg/kg; 5 of 6 rats died after 5 doses at the highest level, 1 died after 10 doses at 1,035 mg/kg, and no animal died at the lowest dose. At autopsy, focal cell hypertrophy and hyperplasia of the liver were seen [NRC 1977]. Rats were fed bromacil at 50, 500, 2,500, 5,000, 6,000, or 7,000 ppm for 90 days; those in the 5,000-ppm or higher groups developed hyperthyroidism [NRC 1977]. In another study, rats were fed bromacil at 50, 250, or 1,250 ppm for 2 years; those in the 1,250-ppm group developed hyperplasia of the thyroid, and one female rat also developed a follicular adenoma [NRC 1977]. When pregnant rats were exposed by inhalation to 38 mg/m^3 (3.8 ppm) for 2 hr/day on gestation days 7 through 14, they developed reproductive, embryotoxic, and developmental effects [NIOSH 1991]. Conversely, rabbits that ingested diets containing 50 to 250 ppm bromacil during days 8 through 16 of pregnancy delivered normal pups. A three-generation rat study also demonstrated a lack of induced developmental toxicity [NLM 1992]. Contradictory mutagenicity results have been published for bromacil [NLM 1992]. A 2-yr chronic dietary study in rats did not result in cancer induction but did demonstrate that bromacil caused thyroid hyperplasia [NRC 1977]. All rats exposed to 4,800 mg/m^3 (480 ppm) bromacil for 4 hr survived [ACGIH 1991a].

2. *Effects on humans*: Bromacil is known to cause eye, nose, and throat irritation in workers handling formulations containing this substance. Skin irritation has also been reported [NLM 1992; NJDH 1985]. There are no reports of bromacil-induced systemic toxicity.

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to bromacil dust can cause redness and itching of the eyes, runny nose, scratchy throat, and redness, dryness, and cracking of the skin.

2. *Chronic exposure*: No signs or symptoms of chronic bromacil exposure have been reported.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or to concentrated solutions, vapors, mists, or aerosols of bromacil. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of bromacil are inhaled move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromacil or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations involve bromacil and may result in worker exposures to this substance:

—Manufacture or formulation of bromacil

—Use of bromacil as a herbicide to control annual and perennial grasses and broadleaf weeds

—Use of bromacil on noncrop lands as a nonselective herbicide and on a few crops (pineapple and citrus) as a selective herbicide

The following methods are effective in controlling worker exposures to bromacil, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromacil, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromacil at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or upper respiratory tract diseases.

- **Periodic medical examinations and biological monitoring.**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromacil exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromacil on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for bromacil.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromacil is determined by using a midget impinger containing 15 ml of ethylene glycol. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 50 liters is collected. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet detector. This method is described in the OSHA Computerized Information System [OSHA 1990] and in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If bromacil contacts the skin, workers should wash the affected areas with soap and water.

Clothing and shoes contaminated with bromacil should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of bromacil, particularly its potential to cause irritation.

A worker who handles bromacil should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromacil is handled, processed, or stored.

STORAGE

Bromacil should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of bromacil should be protected from physical damage and should be stored separately from strong acids and heat. Because containers that formerly contained bromacil may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromacil, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

5. For dry spills, use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

6. Absorb any spilled liquid containing bromacil with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Bromacil is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of bromacil; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromacil emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although bromacil is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromacil exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with bromacil. One source suggests wearing protective gloves and clothing when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by formulations containing bromacil. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to bromacil.

If bromacil is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which bromacil might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromacil. Contact lenses should not be worn if the potential exists for bromacil exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMINE

INTRODUCTION

This guideline summarizes pertinent information about bromine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Br_2

- **Synonyms**

Caswell No. 112

- **Identifiers**

1. CAS No.: 7726-95-6
2. RTECS No.: EF9100000
3. DOT UN: 1744 59
4. DOT label: Corrosive

- **Appearance and odor**

Bromine is a heavy, noncombustible, red-brown fuming liquid with an irritating and suffocating odor. The odor threshold is reported to be 0.05 to 3.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Atomic number: 35
2. Molecular weight: 159.8
3. Boiling point (at 760 mm Hg): 58.8°C (137.8°F)
4. Specific gravity (water = 1): 3.1 at 20°C (68°F)
5. Vapor density (air = 1 at boiling point of bromine): 3.5
6. Melting point: −7.2°C (18.9°F)
7. Vapor pressure: 172 mm Hg at 20°C (68°F); 100 mm Hg at 9.3°C (48.7°F)
8. Solubility: Very slightly soluble in water; freely soluble in alcohol, ether, carbon tetrachloride, carbon disulfide, aqueous solutions of bromides, chloroform, and concentrated hydrochloric acid.
9. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Bromine emits toxic fumes when it is heated or in contact with steam or water.
2. Incompatibilities: Bromine is a powerful oxidizer; in contact with organic or other readily oxidizable materials, it may cause fires and explosions. Contact of liquid bromine with aqueous ammonia or with metals may cause violent reactions. Anhydrous bromine reacts violently with aluminum, titanium, mercury, or potassium. Bromine is also incompatible with alkali hydroxides, arsenites, carbonyls, alcohols, ferrous and mercurous salts, hypophosphites, and many other substances.
3. Hazardous decomposition products: Toxic fumes may be released in a fire involving bromine.
4. Special precautions: Bromine attacks some coatings and some forms of plastic and rubber. This substance corrodes iron, steel, stainless steel, and copper.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to bromine; however, it is a strong oxidizer and accelerates the burning of combustibles. The heat of such reactions may cause nearby combustible materials to ignite.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or alcohol foam to fight fires involving bromine. Because bromine can react with steam or with small amounts of water, containers should be cooled and surrounding fires should be extinguished by flooding with large amounts of water. Anhydrous ammonia vapor released from a safe distance can be used to neutralize large quantities of bromine vapor; do ***not*** use aqueous ammonia because it may react violently with liquid bromine.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromine. Chemical protective clothing that is specifically recommended for bromine may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromine is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 0.3 ppm (2 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as an 8-hr TWA and 0.3 ppm (2 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromine a threshold limit value (TLV) of 0.1 ppm (0.7 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (2 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of severe irritation of the eyes, mucous membranes, lungs, and skin associated with exposure to bromine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to bromine can occur through eye or skin contact, inhalation, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals*: Bromine is a corrosive and severe irritant to the eyes, skin, mucous membranes, and respiratory tract in animals and can be rapidly fatal when inhaled. The lowest observed lethal concentration (LC_{Lo}) is 140 ppm for 7 hr in cats and guinea pigs and 180 ppm for 6.5 hr in rabbits [NIOSH 1991]. Cats, rabbits, and guinea pigs exposed to 180 ppm for 7 hr developed severe eye irritation with clouding of the cornea, severe irritation of the respiratory tract, and difficult breathing; at 23 ppm, however, the irritation and dyspnea was mild [NLM 1992]. Guinea pigs and rabbits exposed to 300 ppm for 3 hr developed lung edema, pseudomembranous deposits on the trachea and bronchi, and hemorrhages of stomach mucosa. Animals that died several days after this exposure showed evidence of bronchopneumonia and central nervous system disturbances at autopsy [Clayton and Clayton 1981]. The 2-hr and 9-min LC_{50}s for mice are 240 and 750 ppm, respectively [ACGIH 1991a; NLM 1992]. Rats, mice, and rabbits inhaling 0.2 ppm of bromine for 4 months showed disturbances in respiratory, endocrine, and nervous system functioning; exposure to 0.02 ppm for the same interval caused no adverse effects [NLM 1992]. Rats fed 0.01 mg/kg bromine for 6 months showed changes in conditional reflexes and in several blood indices.

2. *Effects on Humans*: Bromine is corrosive to the eyes, skin, mucous membranes, and respiratory tract in humans. Eye contact can result in severe, painful, and destructive burns of the eyes [Sittig 1985; AIHA 1978]. Brief contact of the skin with liquid bromine causes vesicles and pustules, and prolonged contact leads to deep, painful burns that ulcerate and are slow to heal [Sittig 1985; Clayton and Clayton 1981]. Repeated contact of the skin with bromine in liquid or vapor form may cause dermatitis and halogen-acne [Rom 1983; Deichmann and Gerarde 1969]. Inhalation of airborne concentrations below 1 ppm causes tearing of the eyes; exposure to 4 ppm can be tolerated for only 30 to 60 min; 10 ppm induces respiratory damage and is considered immediately dangerous to life or health; and 30 ppm would cause death in a short time [Clayton and Clayton 1981; NIOSH 1987b; NLM 1992]. Acute nonlethal exposures can also induce coughing, nosebleed, feelings of oppression, dizziness, headache, and delayed onset of abdominal pain and measles-like dermal eruptions [NLM 1992]. Pulmonary edema may occur after several hours, and high concentrations can cause death from corrosive burns of the lung [Parmeggiani 1983; Sittig 1985]. The inhalation LC_{Lo} in humans is 1,000 ppm [NIOSH 1991]. The lowest lethal oral dose is estimated to be 14 mg/kg [NIOSH 1991]. Ingestion of the liquid produces corrosive tissue burns, mouth and esophageal pain, vomiting, diarrhea, shock (hypotension, tachycardia, cyanosis), headache, dizziness, delirium, collapse, and stupor. Death can result from glottic or pulmonary

edema or aspiration pneumonia. Survivors can develop esophageal and pyloric stenoses [NLM 1992]. Regular exposure to 0.3 to 0.6 ppm for 1 year has induced headache, heart-area chest pain, irritability, anorexia, joint pain, and dyspepsia. Continued exposure for 5 to 6 years can cause loss of corneal reflexes, pharyngitis, vegetative disorders, thyroid hyperplasia and dysfunction, cardiovascular disorders (myocardial degeneration and hypotension), digestive tract secretory disorders, and inhibition of leucopoiesis and leucocytosis [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to bromine can cause irritation or corrosion of contacted tissues, tearing, corneal clouding, dizziness, headache, pulmonary edema, dyspnea, nosebleeds, coughing, bronchopneumonia, central nervous system disturbances, abdominal pain, diarrhea, altered conditioned reflexes, delirium, collapse, and death. Survivors of ingestion incidents can develop esophageal and pyloric stenoses.

2. *Chronic exposure*: Chronic exposure to bromine can cause contact irritation, slow healing, painful acne-like skin eruptions, headache, heart pain, irritability, anorexia, joint pain, dyspepsia, loss of corneal reflexes, pharyngitis, vegetative disorders, thyroid dysfunction, and cardiovascular and digestive disorders.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of bromine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of bromine are inhaled, move the victim to fresh air ***immediately***. If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromine or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve bromine and may result in worker exposures to this substance:

—Manufacture of ethylene dibromide, an anti-knock gasoline additive

—Use of bromine as a solvent

—Manufacture of pesticides

—Use of bromine in flame retardants for the plastics, fabric, and fiber industries

—Use of bromine as a sanitizing, disinfecting, bleaching, and water-purifying agent

—Manufacture of organic and inorganic compounds for use in photographic films and papers, sedatives, inks, anesthetics, hydraulic fluids, pharmaceuticals, fungicides, laboratory reagents, dyes and dyestuffs, war gases, refrigerating and dehumidifying agents, and hair-waving preparations

—Use of bromine as a bleaching agent for silks and other fabrics, as a shrink-proofing agent for wool, as a desizing agent for cotton, and in gold extraction

The following methods are effective in controlling worker exposures to bromine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromine on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for bromine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromine is determined by using a midget fritted-glass bubbler containing 10 ml of a standard eluent carbonate-bicarbonate solution (0.003 M $NaHCO_3$ to 0.0024 M Na_2CO_3). Samples are collected at a maximum flow rate of 0.5 liter/min until a recommended air volume of 30 liters is collected. (Sampling may continue up to a maximum volume of 120 liters.) Analysis is conducted by ion chromatography. The limit of detection for this procedure is 6.7 $\mu g/m^3$ for a 30-liter sample. This method is described in Method ID-108 of the *OSHA Analytical Methods Manual* [OSHA 1985]. An alternate method uses a silver membrane filter for sample collection, and ion chromatography for analysis with a limit of detection of 1.6 µg of bromine per sample. This method is described in Method 6011 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If bromine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then soak the affected areas in a 10% aqueous thiosulfate solution. Get medical help immediately.

Clothing and shoes contaminated with bromine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of bromine, particularly its potential for being corrosive to the eyes, skin, and respiratory tract.

A worker who handles bromine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromine or a solution containing bromine is handled, processed, or stored.

STORAGE

Bromine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of bromine should be protected from physical damage and should be stored separately from combustibles, organic or other readily oxidizable materials, ammonia, aluminum, titanium, mercury, potassium, alkali hydroxides, arsenites, ferrous and mercurous salts, hypophosphites, heat, sparks, direct sunlight, and open flame. Bromine should be stored at temperatures above −6.7°C (19.9°F) to prevent freezing; heating containers of bromine above atmospheric temperatures may rupture the containers. Because containers that formerly contained bromine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

Before bromine is handled in the workplace, an emergency plan for dealing with emergency spills or leaks of this substance must be developed. In the event of a spill or leak involving bromine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Stay upwind of the spill or leak area to the extent possible.

4. Neutralize small liquid spills by pouring a hypo solution (sodium thiosulfate or limewater) over them; the spilled material can then be absorbed with sand or other noncombustible absorbent material and placed in a covered container for later disposal.

5. Neutralize large liquid spills with a solution of potassium carbonate, sodium carbonate, or sodium bicarbonate; or build a dike far ahead of the spill to contain the bromine for later reclamation or disposal.

6. Neutralize bromine vapors in air by carefully releasing anhydrous ammonia gas (do ***not*** use aqueous ammonia gas).

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

If 500 lb or more of bromine is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for bromine is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although bromine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987c] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with bromine. Rubber boots, gloves, aprons, and full-body covering are recommended. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon$^{®}$ has been tested against permeation by bromine and may provide good-to-excellent resistance for more than 4 but fewer than 8 hr. Polyethylene and natural rubber have been tested against bromine and have demonstrated poor resistance to permeation by bromine.

If bromine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which bromine might contact the eyes (e.g., through contact with the vapor or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromine. Contact lenses should not be worn if the potential exists for bromine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMINE PENTAFLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about bromine pentafluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

BrF_5

- **Synonyms**

Bromine fluoride

- **Identifiers**

1. CAS No.: 7789-30-2
2. RTECS No.: EF9350000
3. DOT UN: 1745 44
4. DOT label: Oxidizer

- **Appearance and odor**

Bromine pentafluoride is a reactive, colorless or pale yellow, fuming liquid at temperatures below 40.3°C (104.5°F); it has a pungent odor and is not flammable. The odor threshold is unknown. At temperatures above 40.3°C (104.5°F), it is a colorless, pungent, and corrosive gas. It is shipped in compressed gas cylinders under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 174.92
2. Boiling point (760 mm Hg): 40.5°C (104.9°F)
3. Specific gravity (water = 1): 2.48 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of bromine pentafluoride): 6.05
5. Melting point: −60.5°C (−76.9°F)
6. Vapor pressure at 20°C (68°F): 328 mm Hg
7. Solubility: Reacts violently with water
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Bromine pentafluoride is stable under normal handling and storage procedures.

2. Incompatibilities: Bromine pentafluoride is a highly reactive compound; it reacts with every known element except the inert gases, nitrogen, and oxygen. Bromine pentafluoride is incompatible with acids, halogens, arsenic, selenium, alkaline halides, sulfur, iodine, glass, metallic halides, metal oxides, and metals (except copper, stainless steel, nickel, and Monel®). Fire or explosion may result from contact of bromine pentafluoride with combustibles or organic matter at room temperature, and contact of this substance with water produces an explosion.

3. Hazardous decomposition products: Toxic gases (such as hydrogen fluoride and hydrogen bromide) may be released in a fire involving bromine pentafluoride.

4. Special precautions: Even under mild reaction conditions, bromine pentafluoride attacks organic compounds vigorously, often causing an explosion.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to bromine pentafluoride.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air: Not applicable

4. Extinguishant: Avoid contact of this material with water. However, water may be used if large amounts of combustible material are involved in the fire and if firefighters can protect themselves by barriers or distance from the violent reaction of bromine pentafluoride and water. Fires involving bromine pentafluoride and small amounts of combustibles may be smothered using a carbon dioxide or dry chemical extinguishant.

Fires involving bromine pentafluoride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of bromine pentafluoride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out; do not get water inside the containers. Stay away from the ends of containers. Runoff to sewers may create a fire or explosion hazard. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromine pentafluoride. Chemical protective clothing that is specifically recommended for bromine pentafluoride may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromine pentafluoride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromine pentafluoride is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromine pentafluoride a threshold limit value (TLV) of 0.1 ppm (0.7 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation, corneal necrosis, and systemic effects associated with exposure to bromine pentafluoride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to bromine pentafluoride can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Acute exposure to bromine pentafluoride is corrosive to the eyes, skin, mucous membranes, and upper respiratory tract, chronic exposure is toxic to the liver and kidneys. Experimental animals (species not identified) exposed to a 500-ppm concentration of bromine pentafluoride vapor immediately exhibited the following signs of acute distress: swollen eyelids, tearing, gasping, corneal cloudiness, and excessive salivation; reducing the concentration to 100 ppm produced these signs after an exposure of 3 min [ACGIH 1991a]. Exposure to 50 ppm caused death in these animals after 30 min [ACGIH 1991a]. At autopsy, animals chronically exposed to bromine pentafluoride at concentrations above 3 ppm showed toxic hepatosis and severe nephrosis, as well as severe respiratory involvement [ACGIH 1991a].

2. *Effects on Humans*: Bromine pentafluoride is a severe pulmonary irritant and is also intensely corrosive to the skin, eyes, and mucous membranes of humans in either the liquid or vapor state [Genium 1986]. Exposure to high (not further specified) concentrations are usually fatal; death is caused by respiratory damage and pulmonary edema [Braker and Mossman 1980]. Exposure to a concentration of 5 to 10 ppm is irritating to the eyes, nose, and throat; based on effects seen in animals, chronic exposure may cause liver, kidney, and lung damage [Braker and Mossman 1980; Genium 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to bromine pentafluoride can cause redness and tearing of the eyes, coughing, breathing difficulty, and a burning sensation of the eyes, nose, and throat. Direct contact of this substance with the eyes or skin can cause severe thermal and chemical burns and tissue destruction.

2. *Chronic exposure*: On the basis of effects seen in animals, long-term exposure to low levels of this substance may cause pain in the abdomen; enlargement of the liver;

blood, pus, or protein in the urine; jaundice; and other signs of lung, liver, or kidney damage.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of bromine pentafluoride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of bromine pentafluoride are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromine pentafluoride or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of bromine pentafluoride may result in worker exposures to this substance:

—Use as an oxidizer in liquid rocket propellant combinations and in chemical synthesis

—Use as a fluorinating agent in isotope enrichment and in fuel-element reprocessing

The following methods are effective in controlling worker exposures to bromine pentafluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers

for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromine pentafluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and lungs. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromine pentafluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with liver, kidney, or lung diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromine pentafluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromine pentafluoride on the liver, kidneys, and lungs. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for bromine pentafluoride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to bromine pentafluoride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromine pentafluoride is determined by using a silica gel tube (Supelco ORBO 53 or equivalent). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 48 liters is collected. Analysis is conducted by ion chromatography. This method is included in the *OSHA Chemical Information Manual* [OSHA 1987] and is based on OSHA Method ID-108.

PERSONAL HYGIENE

If bromine pentafluoride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water. Washing should be continued until the liquid is completely removed from the skin. The burned area should then be immersed in an ice bath, or a cold compress should be applied to the affected area.

Clothing and shoes contaminated with bromine pentafluoride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of bromine pentafluoride, particularly its potential for being corrosive to the skin and eyes.

A worker who handles bromine pentafluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromine pentafluoride is handled, processed, or stored.

STORAGE

Bromine pentafluoride should be isolated from other stored materials; it must be stored in a cool, dry, well-ventilated area in tightly sealed gas cylinders that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Extreme caution should be used when handling this material. Containers of bromine pentafluoride should be protected from physical damage and separated from combustible or organic materials, water, acids, halogens, arsenic, selenium, alkaline halides, sulfur, iodine, glass, metallic halides, metal oxides, metals (except for copper, stainless steel, nickel, and Monel), heat, sparks, and open flame. Bromine pentafluoride reacts with every known element except nitrogen, oxygen, and the inert gases. Because containers that formerly held bromine pentafluoride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromine pentafluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Remove leaking cylinder(s) to a safe place if feasible; attempt to stop the leak if it is possible to do so without risk.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Bromine pentafluoride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of bromine pentafluoride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromine pentafluoride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although bromine pentafluoride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromine pentafluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with bromine pentafluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to bromine pentafluoride permeation; however, sources recommend the use of acid suits, aprons, boots, neoprene gloves, and other appropriate protective clothing when handling this substance. Since specific test data are not available for bromine pentafluoride, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to bromine pentafluoride.

Safety glasses, goggles, or face shields should be worn during operations in which bromine pentafluoride might contact the eyes (e.g., through vapors or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromine pentafluoride. Contact lenses should not be worn if the potential exists for bromine pentafluoride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMOFORM

INTRODUCTION

This guideline summarizes pertinent information about bromoform for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CHBr_3$

- **Synonyms**

Tribromomethane, methenyl tribromide, methyl tribromide

- **Identifiers**

1. CAS No.: 75-25-2
2. RTECS No.: PB5600000
3. DOT UN: 2515 58
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Bromoform is a nonflammable, colorless-to-dark-brown, fuming, volatile liquid with a suffocating chloroformlike odor; it may form hexagonal crystals at 6° to 7°C (43° to 45°F). The odor threshold is reported to be 1.3 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 252.8
2. Boiling point (at 760 mm Hg): 149° to 150°C (300.2° to 302°F)
3. Specific gravity (water = 1): 2.9 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of bromoform): 8.7
5. Melting point: 8.3°C (46.9°F)
6. Vapor pressure at 20°C (68°F): 5 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, benzene, chloroform, ether, petroleum ether, acetone, and oils
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires and explosions may result from contact of bromoform with chemically active metals (sodium, potassium, powdered aluminum, zinc, magnesium, lithium), calcium, acetone, or strong caustics (such as potassium hydroxide).
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide, bromine, hydrogen bromide, and bromine oxides) may be released in a fire involving bromoform.
4. Special precautions: Liquid bromoform attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to bromoform; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air (% by volume): Not applicable

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4. Extinguishant: Bromoform itself does not burn; use an extinguishant that is suitable for the material involved in the surrounding fire.

Fires involving bromoform should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromoform. Chemical protective clothing that is specifically recommended for bromoform may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromoform.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromoform is 0.5 ppm (5 mg/m^3) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 ppm (5 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromoform a threshold limit value (TLV) of 0.5 ppm (5.2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of irritation and liver damage associated with exposure to bromoform.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to bromoform can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Bromoform is an irritant of the eyes, skin, and respiratory tract; a central nervous system depressant; and a liver and kidney toxin. The application of undiluted bromoform to the eyes of rabbits caused moderate irritation that healed within 1 or 2 days. Rabbits also acutely exposed dermally to undiluted bromoform (2,000 mg/kg) developed moderate skin irritation but did not die [Clayton and Clayton 1981]. Rabbits exposed to 1,070 to 1,270 ppm for an unspecified duration developed narcosis [Clayton and Clayton 1981]. A dog exposed for 1 hr to approximately 7,000 ppm experienced deep narcosis followed by death [ACGIH 1991a]. The oral LD_{50}s for male and female rats were 1,388 and 1,147 mg/kg, respectively. Exposure of rabbits to 243 ppm for 10 days resulted in functional changes in the central nervous system, liver, and kidneys plus vascular and dystrophic changes [Clayton and Clayton 1981]. Rats exposed to 24 ppm for 4 hr/day for 2 months developed disorders in liver prothrombin synthesis and glycogenesis as well as reduced renal filtration capacity [NLM 1991]. Bromoform was mutagenic when tested in three strains of *Salmonella typhimurium* [ACGIH 1991a]. Carcinogenicity bioassays were performed with mice and rats treated by gavage with various doses of bromoform for 5 days/week during 103 weeks. Although the male and female rats in these bioassays showed an increased incidence of adenomatous polyps or adenocarcinomas of the large intestine, the mice were unaffected by treatment [NTP 1989]. Mice given repeated intraperitoneal injections of bromoform developed a significantly increased incidence of pulmonary adenomas [Theiss et al. 1977].

2. *Effects on Humans*: Bromoform has both narcotic and irritant effects in humans. Exposure to the vapor at unspecified concentrations causes irritation of the eyes, respiratory tract, pharnyx, and larnyx [Proctor et al. 1988]. Prolonged contact with the skin may lead to skin burns [NLM 1991]. Accidental ingestion of bromoform has produced central nervous system depression with coma and loss of reflexes; small doses have led to listlessness, headache, and vertigo [ACGIH 1991a].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to bromoform can cause irritation, tearing, headache, dizziness, vertigo, digestive symptoms, weight loss, excessive salivation, lethargy, sedation, amnesia, shock, convulsions, anesthesia, pulmonary edema, respiratory failure, and death.

2. *Chronic exposure*: No signs or symptoms of chronic bromoform exposure have been reported.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of bromoform. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of bromoform are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromoform or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of bromoform may result in worker exposures to this substance:

—Use as a reagent for graphite ore fractionation and as a heavy liquid flotation agent in mineral separation for sedimentary petrographical surveys, geological assays, and purification of materials such as quartz

—Use in the shipbuilding, aircraft, and aerospace industries

—Use as a solvent for waxes, greases, oils, and fats

—Use as an ingredient in fire-resistant chemicals and gauge fluids

—Use as an ingredient in pharmaceuticals and medicinal products such as antiseptics, sedatives, and cough suppressants

The following methods are effective in controlling worker exposures to bromoform, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromoform, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system, liver, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromoform at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with central nervous system, liver, kidney, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromoform exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromoform on the central nervous system, liver, kidneys, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Inorganic bromide can be detected in the serum of bromine-exposed workers. Some sources suggest that the serum bromide concentration in bromoform-exposed workers should not exceed 15 to 30 mg/liter of serum. However, because few data correlate airborne exposure concentrations with serum bromide concentrations, no biological monitoring test acceptable for routine use has yet been developed for bromoform.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromoform is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 5 µg per sample. This method is described in Method 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If bromoform contacts the skin, workers should flush the affected areas immediately with plenty of water and then wash thoroughly with soap and water.

Clothing contaminated with bromoform should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of bromoform, particularly its potential for causing eye and respiratory tract irritation.

A worker who handles bromoform should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromoform or solutions containing bromoform are handled, processed, or stored.

STORAGE

Bromoform should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of bromoform should be protected from physical damage and should be stored separately from caustic alkalies, chemically active metals (such as sodium, potassium, powdered aluminum, zinc, magnesium, and lithium), calcium, acetone, heat, sparks, and open flame. Because containers that formerly contained bromoform may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromoform, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. Absorb small spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

5. For large spills, build dikes far ahead of the spill to contain the bromoform for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Bromoform is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for bromoform is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of bromoform per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromoform emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Bromoform is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and it has been assigned EPA Hazardous Waste No. U225. Bromoform is approved for land disposal as long as the concentration of bromoform in the waste or treatment residual does not exceed 15 mg/kg. Bromoform also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromoform exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with bromoform. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by bromoform and have demonstrated protection for periods greater than 8 hr: polyvinyl alcohol and Viton®. Butyl rubber has demonstrated questionable resistance to permeation by bromoform. Natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by bromoform.

If bromoform is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which bromoform might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromoform. Contact lenses should not be worn if the potential exists for bromoform exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BUTADIENE (1,3-BUTADIENE)

INTRODUCTION

This guideline summarizes pertinent information about butadiene (1,3-butadiene) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_4H_6

- **Structure**

$CH_2{=}CH\text{-}CH{=}CH_2$

- **Synonyms**

1,3-Butadiene, trans-butadiene, bivinyl, divinyl, erythrene, vinylethylene, biethylene, butadiene monomer, pyrrolylene, 1-methylallene

- **Identifiers**

1. CAS No.: 106-99-0
2. RTECS No.: EI9275000
3. DOT UN: 1010 17 (inhibited butadiene)
4. DOT label: Flammable Gas (inhibited butadiene)

- **Appearance and odor**

Butadiene is a colorless, flammable gas with a mild aromatic odor. It is shipped under its own vapor pressure as a liquefied gas. The odor threshold is reported to be 1.1 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 54.1
2. Boiling point (760 mm Hg): −4.4°C (24°F)
3. Specific gravity (water = 1): 0.62 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of butadiene): 1.9
5. Melting point: −108.9°C (−164.0°F)
6. Vapor pressure at 21°C (69.8°F): 1,840 mm Hg
7. Solubility: Insoluble in water; soluble in alcohol, ether, acetone, and benzene
8. Evaporation rate: Not applicable; butadiene is a gas.

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame. When exposed to air, butadiene may form explosive peroxides.
2. Incompatibilities: Fires, explosions, or hazardous polymerization may result from contact of butadiene with air, strong oxidizers, ozone, nitrogen dioxide, copper, copper alloys, phenol, chlorine dioxide, crotonaldehyde, or a free radical polymerization initiator such as hydroquinone.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving butadiene.
4. Special precautions: Butadiene is self-reactive. To prevent hazardous polymerization, an inhibitor must be added to the butadiene and the concentration of inhibitor (such as tert-butylcatechol) must be monitored to ensure that it remains at effective levels at all times.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to butadiene.

1. Flash point: −156°F (105°C)
2. Autoignition temperature: 420°C (788°F)

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3. Flammable limits in air (% by volume): Lower, 2.0; upper, 12.0

4. Extinguishant: Butadiene is a flammable gas. To extinguish a fire involving this substance, the flow of gas must be stopped. Fires involving butadiene should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of butadiene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving butadiene. Firefighters' protective clothing may not provide protection against permeation by butadiene.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for buta-diene is 1,000 ppm (2,200 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A]. However, OSHA has published a proposed rule on occupational exposure to butadiene that would reduce the PEL to 2 ppm as a TWA and 10 ppm as a short-term exposure limit (STEL) [55 FR 32736, August 10, 1990]. A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has recommended that butadiene be considered a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration [NIOSH 1984a, 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated butadiene an A2 substance (suspected human carcinogen) and has assigned butadiene a threshold limit value (TLV) of 10 ppm (22 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The current OSHA limit is based on the risk of irritation and narcosis associated with exposure to butadiene and does not take into account the possible carcinogenic effects of this substance. The proposed OSHA PEL and NIOSH REL are based on butadiene's potential occupational carcinogenicity and reproductive toxicity. The ACGIH TLV is based on potential occupational carcinogenicity.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to butadiene can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Butadiene is an irritant of the eyes and mucous membranes, and it is a narcotic at high concentrations. This substance is also a carcinogen and reproductive toxin in experimental animals. The 2-hr LC_{50} in rats is 270 g/m^3 (129,000 ppm) [NIOSH 1991]. Rabbits exposed for 8 to 10 min at 200,000 to 250,000 ppm were deeply anesthetized but recovered completely after exposure ceased. If the exposure was continued for 25 to 35 min, the animals died [ACGIH 1991a]. Inhalation of 625 or 1,250 ppm butadiene for 6 hr/day, 5 days/week for 6 weeks caused nonneoplastic effects in mice at several organ sites (ovaries, testes, nasopharynx, lung, and liver) [NIOSH 1984a]. Rats, guinea pigs, rabbits, and a dog exposed to butadiene concentrations ranging from 600 to 6,700 ppm for 7.5 hr/day, 6 days/week for 8 months developed no significant toxic effects [ACGIH 1991a; Proctor et al. 1988]. Inhalation exposure to butadiene at 200 ppm was toxic to pregnant rats and retarded embryonic growth and development; exposure at 8,000 ppm during pregnancy caused a significant increase in major skeletal abnormalities in the offspring [Proctor et al. 1988; ACGIH 1991a]. Butadiene has caused cancers in the mammary glands, uterus, ovaries, testes, thyroid gland, pancreas, liver, Zymbal gland, heart, lungs, lymph system, and hematopoietic system in rats and mice chronically exposed to this substance in inhalation bioassays [NIOSH 1984a]. On this basis, the International Agency for Research on Cancer (IARC) has concluded that butadiene is an animal carcinogen [IARC 1986].

2. *Effects on Humans*: Exposure to butadiene causes irritation of the eyes, mucous membranes, upper respiratory tract, and skin in exposed workers [Cralley and Cralley 1985; ACGIH 1991a]. Volunteers exposed to butadiene at 2,000 ppm experienced irritation of the eyes, nose, throat, and skin [NIOSH 1984a]. In contact with the skin, the liquid may cause frostbite [NIOSH 1984a]. Epidemiological studies of workers exposed to butadiene, styrene, and benzene at two styrene-butadiene rubber facilities (with average

butadiene exposures of 1.24 and 13.5 ppm, respectively) have shown an increased, but not statistically significant, risk of mortality from lymphatic and hematopoietic system cancer and from leukemia [NIOSH 1984a]. IARC has stated that evidence is insufficient to conclude that butadiene is a human carcinogen [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to butadiene can cause irritation of the eyes, nose, and throat, with redness and tearing of the eyes, runny nose, and cough. Skin contact with butadiene in liquid form may cause burns or frostbite. At high concentrations, butadiene causes blurred vision, nausea, fatigue, headache, dizziness, rapid breathing, decreased blood pressure and pulse, diminished mental alertness, muscular incoordination, unconsciousness, respiratory paralysis, and death.

2. *Chronic exposure*: Prolonged or repeated skin contact with butadiene can induce dermatitis. On the basis of effects seen in animals, butadiene should be considered a potential carcinogen.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***; if tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia persists, get medical attention as soon as possible.

2. *Skin exposure*: If frostbite has occurred, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If frostbite has ***not*** occurred, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve butadiene and may result in worker exposures to this substance:

—Manufacture of styrene-butadiene-rubber (SBR) elastomer, polybutadiene elastomer, neoprene elastomer, nitrile elastomer, styrene-butadiene (SB) copolymer, and acrylonitrile-butadiene-styrene (ABS) resins, which are used as reinforcing and stiffening agents for rubbers

—Manufacture of high-impact polystyrene containing SBR/polybutadiene elastomer and of SBR foams

—Molding and vulcanizing operations that process synthetic rubber products from SBR

—Use of butadiene in latexes and resins to make carpet backing, paper coatings, high-impact-resistant pipes and parts for automobiles, appliances, business machines, telephones, and recreational vehicles

—Manufacture of tires, hoses, belts, gaskets, seals, and oil-resistant textile and paper products

—Manufacture of adiponitrile; cyclo-olefins; 1,4-hexadiene tetramethylene sulfone; tetrahydrophthalic anhydride; hexamethylenediamine; ethylidenenorbornene; and 1,5,9-cyclodecatriene

—Use of butadiene in the Diels-Alder condensation reaction for synthesis of compounds

—Use of butadiene in food wrappings, the latex paint industry, rocket fuels, pesticides, and fungicides

The following methods are effective in controlling worker exposures to butadiene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrylic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to butadiene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of butadiene on the respiratory tract and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for butadiene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to butadiene may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne butadiene is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh) coated with 10% (w/w) 4-tert-butylcatechol. Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 3 liters is collected. The sample is then treated with carbon disulfide to extract the butadiene. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.11. The OSHA method is described in the OSHA Computerized Information System [OSHA 1990] and in Method 56 of the *OSHA Analytical Methods Manual*

[OSHA 1985]. NIOSH has a similiar method for butadiene [NIOSH 1984b]. OSHA Method 56 is compared with NIOSH Method 1024 in the NIOSH comments on the proposed rule for 1,3-butadiene [NIOSH 1990].

PERSONAL HYGIENE

If liquid butadiene contacts the skin, frostbite may occur. Workers should flush the affected areas immediately with plenty of tepid water and then wrap the affected part in a warm dressing. Medical aid should be obtained immediately.

Clothing contaminated with liquid butadiene should be removed immediately.

A worker who handles butadiene cylinders should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where butadiene cylinders are handled, processed, or stored.

STORAGE

Butadiene should be stored in a cool, dry, well-ventilated area in tightly sealed and pressurized containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside, isolated, or detached storage is preferred; inside storage should be in a noncombustible location. Containers of butadiene should be stored upright and should not be stacked. Containers of butadiene should be protected from physical damage and should be stored separately from oxygen, chlorine, phenol, chlorine dioxide, crotonaldehyde, copper, copper alloys, oxidizers, heat, sparks, and open flame. The manufacturer's recommendations regarding shelf life, rotation of inventory, and monitoring of levels of inhibitor should be followed rigorously. Only nonsparking tools may be used to handle butadiene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained butadiene may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving butadiene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. *Do not touch the spilled material.*
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Isolate the area until the gas has dispersed.
5. If butadiene gas is leaking, stop the flow of gas if it is possible to do so without risk.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore *advised to determine periodically whether new information* is available.

- **Emergency planning requirements**

Butadiene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC *11022*].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of butadiene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of butadiene per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of butadiene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although butadiene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in

Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of butadiene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with butadiene. Protective gloves and clothing are recommended for workers handling this material. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by butadiene and have demonstrated good-to-excellent resistance for periods of greater than 8 hr: butyl rubber and Viton®. Natural rubber, neoprene, and polyvinyl chloride have demonstrated poor resistance to permeation by butadiene. If butadiene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which butadiene might contact the eyes (e.g., through splashes of the liquid). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with liquid butadiene. Contact lenses should not be worn if the potential exists for butadiene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTANE

INTRODUCTION

This guideline summarizes pertinent information about n-butane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_4H_{10}

- **Structure**

$CH_3CH_2CH_2CH_3$

- **Synonyms**

Butane, butyl hydride, diethyl, liquefied petroleum gas, methylethylmethane

- **Identifiers**

1. CAS No.: 106-97-8
2. RTECS No.: EJ4200000
3. DOT UN: 1011 22
4. DOT label: Flammable Gas

- **Appearance and odor**

n-Butane is a colorless gas with no odor, although an odorant is sometimes added to the gas to provide warning of its presence. This gas is commercially available in several grades of purity and in various mixtures (with the isobutane isomer, propane, and/or pentane). n-Butane is usually shipped under pressure as a liquefied gas and is one of the major ingredients in bottled gas.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58.1
2. Boiling point (760 mm Hg): −0.5°C (31.1°F)
3. Specific gravity (water = 1): 0.5788 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butane): 2.07
5. Melting point: −138.4°C (−217.1°F)
6. Vapor pressure at 20°C (68°F): 1,557 mm Hg
7. Solubility: Soluble in water; very soluble in alcohol, ether, and chloroform
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Fire and explosions may result from contact of n-butane with oxidizers. A mixture of n-butane and oxygen will explode on contact with nickel carbonyl in the 20° to 40°C (68° to 104°F) temperature range.

3. Hazardous decomposition products: Acrid smoke and fumes may be released when n-butane undergoes thermal oxidative decomposition.

4. Special precautions: Do not use n-butane around sparking motors or other nonexplosionproof equipment. Ground all lines and equipment used with n-butane.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to n-butane.

1. Flash point: −60°C (−76°F) (closed cup) (liquefied n-butane).
2. Autoignition temperature: 430°C (806°F)

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3. Flammable limits in air (% by volume): Lower, approximately 1.9; upper, approximately 8.4

4. Extinguishant: Stop flow of gas. Use water to keep fire-exposed containers cool and to protect persons effecting the shutoff. If a leak or spill has not ignited, water spray may be used to disperse the gas or vapor and to protect persons attempting to stop the leak.

Fires involving n-butane should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-butane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butane.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butane is 800 ppm (1,900 mg/m^3) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for n-butane of 800 ppm (1,900 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butane a threshold limit value (TLV) of 800 ppm (1,900 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on drowsiness and the risk of narcosis associated with exposure to n-butane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to n-butane can occur through inhalation or eye and skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Contact with liquid n-butane can cause frostbite. This gas is also an anesthetic and asphyxiant in animals at very high concentrations. Although n-butane was mildly to moderately irritating to rabbit skin, it did not produce ocular or respiratory tract irritation [NLM 1992]. However, direct tissue contact with liquid n-butane can cause frostbite [NLM 1992]. Anesthetized dogs concomitantly exposed to 5,000 ppm developed hemodynamic changes (decreased myocardial contractility, stroke volume, cardiac output, and left ventricular and aortic pressures) [Clayton and Clayton 1981]. Dogs exposed to 10,000 ppm for 2 hr or 200,000 ppm for 2 min were hypersensitized to epinephrine-induced ventricular fibrillation. Exposure of dogs to 150,000 to 900,000 ppm for 10 min also caused heart sensitization to epinephrine-induced arrhythmias [NLM 1992]. The anesthetic concentration for n-butane is 250,000 ppm in dogs [NLM 1992] and 220,000 ppm for 1 min or 130,000 ppm for 25 min in mice [Clayton and Clayton 1981]. The 30-min LC_{50} for mice is approximately 285,000 ppm, but the 15-min LC_{50} for rats is about 275,000 ppm [NLM 1992]. n-Butane was not mutagenic in the *Salmonella typhimurium* assay [NLM 1992].

2. *Effects on Humans*: A transient blurring of vision resulted when n-butane was accidently sprayed into the eyes from a cigarette lighter [NLM 1992]. However, contact of the eyes or skin with n-butane gas does not normally cause irritation, but contact with the liquefied form may cause frostbite of the eyes or skin [Clayton and Clayton 1981; Genium 1990]. Exposure to 10,000 ppm for 10 min may lead to drowsiness but does not appear to cause systemic effects [Clayton and Clayton 1981]. A 2-year-old girl developed seizures, hypotension, and recurrent ventricular tachycardia following inhalation of an aerosol spray from a can containing a mixture of n-butane, isobutane, and propane [NLM 1992]. Progressive bilateral pulmonary infiltrates consistent with hydrocarbon pneumonitis developed in a "fire breather" following an inhalation of unignited fumes from a butane lighter. Exposure of volunteers to 1,000 ppm for 8 hr or 500 ppm for 8 hr/day, 5 days/week for 2 weeks did not induce toxicity [ACGIH 1991a]. Intentional inhalation abuse of n-butane for 1 year by a 16-year-old girl caused her to suffer from visual hallucinations, increased irritability, and social withdrawal [NLM 1992]. Exposure to n-butane at very high concentrations can affect the central nervous system, causing narcosis and asphyxiation [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-butane can cause central nervous system depression (drowsiness and lightheadedness), narcosis, and asphyxiation. Contact with liquefied n-butane can cause eye and skin burns (frostbite).

2. *Chronic exposure*: Visual hallucinations, irritability, and social withdrawal have been reported with chronic exposure. Cardiac sensitization may also be possible.

- **Emergency procedures**

[illegible]

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***; if tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the lower and upper eyelids. If irritation, pain, swelling, lacrimation, or photophobia persists, get medical attention as soon as possible.

2. *Skin exposure*: If frostbite has occurred, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If frostbite has ***not*** occurred, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-butane and may result in worker exposures to this substance:

—Use of n-butane as a raw material in the production of motor and aviation fuels

—Use of n-butane as a household fuel, solvent, refrigerant, standby and enricher gas, and propellant in aerosols

—Use of pure grades of n-butane in calibrating instruments

—Use of n-butane as a food additive

—Manufacture of ethylene and butadiene

—Use of n-butane as a special motor fuel for in-plant trucking, where the presence of gasoline vapors is undesirable

The following methods are effective in controlling worker exposures to n-butane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butane.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butane is determined by using two charcoal tubes in series (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the n-butane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If liquefied n-butane contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and should not rub the affected areas.

Workers should not eat, drink, or use tobacco products in areas where n-butane is handled, processed, or stored.

Workers should wash their hands after handling liquefied n-butane.

STORAGE

n-Butane should be stored in a cool, dry, well-ventilated, low-fire-risk area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of n-butane should be protected from physical damage and should be stored separately from oxidizers (including cylinders of oxygen or chlorine), nickel carbonyl, heat, sparks, and open flame. All equipment used with n-butane should be electrically bonded and grounded. Because containers that formerly contained n-butane may still hold product residues, they should be handled appropriately.

LEAKS

In the event of a leak involving n-butane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate potentially explosive atmospheres; supply optimum explosionproof ventilation to disperse the gas.
4. Use self-contained breathing apparatus and protection against contact with the cold liquid to avoid frostbite when attempting to stop the leak.
5. Stop the leak or remove the leaky cylinder or tank to a safe, open area and vent it slowly to empty the container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of n-butane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butane emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-butane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1900.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with n-butane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been shown to provide resistance to liquefied n-butane: neoprene rubber, the combination of nitrile and polyvinyl chloride, and Viton®. Natural rubber, nitrile, and polyvinyl chloride have demonstrated poor resistance to n-butane.

Safety glasses, goggles, or face shields should be worn during operations in which n-butane might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butane. Contact lenses should not be worn if the potential exists for exposure to liquefied n-butane.

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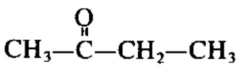
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-BUTANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-butanone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_4H_8O
- **Structure:**



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

- **Synonyms:** Ethyl methyl ketone, MEK, methyl ethyl ketone
- **Identifiers:** CAS 78-93-3; RTECS EL6475000; DOT 1193, label required: "Flammable Liquid"
- **Appearance and odor:** Clear and colorless liquid with an odor like acetone

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72.12
2. Boiling point (at 760 mmHg): 79.6 °C (175 °F)
3. Specific gravity (water = 1): 0.806
4. Vapor density (air = 1 at boiling point of 2-butanone): 2.5
5. Melting point: -86.5 °C (-123.7 °F)
6. Vapor pressure at 20 °C (68 °F): 70 mmHg; at 25 °C (77 °F), 100 mmHg
7. Solubility in water, g/100 g water at 20 °C (68 °F): 25.6
8. Evaporation rate (butyl acetate = 1): 5.7
9. Saturation concentration (approximate) at 20 °C (68 °F): 10.2% (102,000 ppm); at 25 °C (77 °F), 13.2% (132,000 ppm)
10. Ionization potential: 9.48 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., formaldehyde and carbon monoxide) may be released in a fire involving 2-butanone.

- **Flammability**

1. Flash point: -9 °C (16 °F) (closed cup)
2. Autoignition temperature: 515.5 °C (959 °F)
3. Flammable limits in air, % by volume: Lower, 2; upper, 10
4. Extinguishant: Carbon dioxide, dry chemicals, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 5 ppm
2. Eye irritation levels: 200-350 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-butanone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-butanone is 200 parts of 2-butanone per million parts of air (ppm) [590 milligrams of 2-butanone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 200 ppm (590 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 200 ppm (590 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 300 ppm (885 mg/m³) (Table 1).

Table 1.—Occupational exposure limits for 2-butanone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	200	590
NIOSH REL TWA	200	590
ACGIH TLV® TWA	200	590
STEL	300	885

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Butanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute inhalation of 2-butanone by guinea pigs caused narcosis, corneal opacities, emphysema, congestion of the brain, lungs, liver, and kidneys, and death. Inhalation of 2-butanone by pregnant rats caused an increased incidence of reduced lengths and weights in offspring.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 2-butanone can cause headache, dizziness, drowsiness, vomiting, and numbness of the extremities. Irritation of the eyes, nose, and throat can also occur.
2. *Long-term (chronic):* Exposure to 2-butanone can cause dryness and irritation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 2-butanone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-butanone at or below the NIOSH REL (especially if exposure occurs in combination with 2-hexanone). The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis, a history of chronic skin disease, or a history and physical findings consistent with peripheral neuropathy.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-butanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to 2-butanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting 2-butanone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure 2-butanone may also be used if available. A detailed sampling and analytical method for 2-butanone may be found in the *NIOSH Manual of Analytical Methods* (method number 2500).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with 2-butanone.

Workers should be provided with and required to use splash-proof goggles where 2-butanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-butanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-butanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-butanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with 2-butanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-butanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-butanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 2-butanone

Operations	Controls
During spray application of vinyl and acrylic coatings; during mixing of dye solutions; during use in laboratories	Local exhaust ventilation, personal protective equipment
During surface spreading and coating of nitrocellulose and vinyl resins; during mixing, batching, and packaging of surface coating preparations; during forced drying of furniture finishes; during dewaxing; during use as a chemical intermediate	Local exhaust ventilation
During use in the application of adhesives for artificial leather	Dilution ventilation, personal protective equipment
During preparatory formulations of lacquers; during sponge or brush application of solvent for cleaning operations; during mixing of waterproofing compounds	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-butanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-butanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-butanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-butanone gets on the skin, wash it immediately with soap and water. If 2-butanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 2-butanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing 2-butanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from 2-butanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-butanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Butanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-butanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for 2-butanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 3,000 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 3,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 200 ppm (590 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-BUTOXYETHANOL

INTRODUCTION

This guideline summarizes pertinent information about 2-butoxyethanol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{14}O_2$

- **Structure**

$CH_3(CH_2)_3OCH_2CH_2OH$

- **Synonyms**

2-Butoxy-1-ethanol; beta-butoxyethanol; o-butyl ethylene glycol; butyl glycol; butyl oxitol; ethylene glycol monobutyl ether; glycol butyl ether; monobutyl ether of ethylene glycol; n-butoxyethanol; Butyl Cellosolve; Dowanol EB; Ektasolve EB; Gafcol EB; Jeffersol EB; Poly-solv EB; EGBE

- **Identifiers**

1. CAS No.: 111-76-2
2. RTECS No.: KJ8575000
3. DOT UN: 2369 26
4. DOT labels: St. Andrew's Cross; Flammable Liquid

- **Appearance and odor**

2-Butoxyethanol is a clear, colorless liquid with a pleasant, etherlike odor. The odor threshold is reported to be 0.35 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 118.2
2. Boiling point (760 mm Hg): 171°C (340°F)
3. Specific gravity (water = 1): 0.90 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of 2-butoxyethanol): 4.1
5. Melting point: −70°C (−94°F)
6. Vapor pressure at 20°C (68°F): 0.8 mm Hg
7. Solubility: Miscible in water, alcohol, ether, mineral oil, and most organic solvents
8. Evaporation rate (butyl acetate = 1): 0.07

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of 2-butoxyethanol with strong oxidizers or caustics.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving 2-butoxyethanol.
4. Special precautions: 2-Butoxyethanol attacks some coatings and some forms of plastic and rubber; at high temperatures, this substance may attack metallic aluminum.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to 2-butoxyethanol.

1. Flash point: 62°C (143°F) (closed cup)
2. Autoignition temperature: 238°C (460°F)
3. Flammable limits in air (% by volume): Lower, 1.1 at 93°C (200°F); upper, 12.7 at 135°C (275°F)

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4. Extinguishant: Use alcohol foam, carbon dioxide, dry chemical, Halon®, water spray, or fog to fight fires involving 2-butoxyethanol. Do *not* use a solid stream of water because it will scatter and spread the fire.

Fires involving 2-butoxyethanol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of 2-butoxyethanol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving 2-butoxyethanol. Firefighters' protective clothing may not provide protection against permeation by 2-butoxyethanol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-butoxyethanol is 25 ppm (120 mg/m3) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (24 mg/m^3) as a 10-hr TWA for a 40-hr workweek; the REL also bears a "Skin" notation [NIOSH 1990, 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-butoxyethanol a threshold limit value (TLV) of 25 ppm (120 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 2-butoxyethanol [ACGIH 1991b].

• Rationale for limits

The OSHA and ACGIH limits are based on the risk of hematologic and other systemic effects associated with exposure to 2-butoxyethanol. The NIOSH limit is based on tissue irritation, CNS depression, and adverse effects of exposure on the blood and hematopoietic systems.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to 2-butoxyethanol can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: 2-Butoxyethanol is an irritant of the eyes, mucous membranes, and skin; it also causes hemolysis, kidney damage, reproductive effects, immunotoxicity, and embryotoxicity in animals. 2-Butoxyethanol caused severe corneal injury in rabbits [Tyler 1984]. When applied to the skin of rabbits for 4 hr, 2-butoxyethanol caused only mild irritation; extending the period of skin contact increased the degree of irritation [Tyler 1984]. Repeated application of this substance to rabbit skin caused systemic toxicity manifested as reduced body weight gain [Tyler 1984]. The oral LD_{50} is about 530 mg/kg in rats and 490 mg/kg in rabbits [NIOSH 1991]. At autopsy, acutely-poisoned animals exhibited kidney damage, narcotic effects, and breathing difficulty before death [Proctor et al. 1988]. Rats exposed to 245 ppm in air for 6 hr/day for 9 days showed significant depressions in red blood cell counts and hemoglobin concentrations and increases in nucleated erythrocytes, reticulocytes, and lymphocytes [Dodd et al. 1983]. Exposure of rats to 77 ppm in air for 30 hr/week for 90 days caused mild hematologic alterations. Fourteen days after exposure ceased, these hematologic effects were no longer evident [Dodd et al. 1983]. Male rats given 500 or 1,000 mg/kg per day for 4 days by oral gavage showed leukopenia and anemia; testicular atrophy was apparent in animals in the 500-mg/kg group [Grant et al. 1985]. Rats given 222, 443, or 885 mg/kg of 2-butoxyethanol by gavage for 6 weeks (5 days/week) showed a dose-dependent decrease in hemoglobin concentration and red blood cell count; these changes were apparent at all dose levels [Krasavage 1986; Ghanayem et al. 1990]. Teratogenicity studies have shown that 2-butoxyethanol to cause maternal, embryonic, and fetal toxicity in rats at 100 or 200 ppm, and maternal and embryonic toxicity in rabbits at 200 ppm [Tyl et al. 1984].

2. *Effects on Humans*: 2-Butoxyethanol is an irritant of the eyes and upper respiratory tract in humans. After an 8-hr exposure to 195 ppm, volunteers reported eye, nose, and throat discomfort; at 113 ppm for 4 hr, milder symptoms were experienced [Proctor et al. 1988]. Although humans appear to be less sensitive to the hematologic effects of 2-butoxyethanol than rats and mice, human red blood cells exposed in vitro showed increased fragility [Carpenter et al. 1956]. In one case report, a worker experienced two separate episodes of hematuria after being exposed to unspecified concentrations of 2-butoxyethanol and diethylene glycol monobutyl ether [Browning 1971].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to 2-butoxyethanol can cause irritation of the eyes, nose, and throat, with pain and tearing of the eyes, runny nose, and cough; skin irritation with redness and cracking; and narcotic effects with difficult breathing.

2. *Chronic exposure*: Chronic exposure to 2-butoxyethanol can cause dermatitis and hematuria.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2-butoxyethanol. ***Immediately and thoroughly*** flush eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If vapors, mists, or aerosols of 2-butoxyethanol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if 2-butoxyethanol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of 2-butoxyethanol may result in worker exposures to this substance:

—Use as a solvent for nitrocellulose resins and enamels, spray lacquers, quick-drying lacquers, varnishes, varnish removers, grease, oil, albumin, and dry cleaning compounds

—Use as a solvent for paints, printing inks, and dyestuffs and as an ingredient in agricultural chemicals, nonvolatile herbicides, brake oils, detergents for the automobile industry, penetrants, and softeners

—Use as a solvent for "soluble" mineral oils to hold soap in solution and to improve emulsifying properties

—Use as a solvent for protective coatings and metal cleaners

—Use as an agent to prevent spotting in textile printing and dyeing

—Use in production of acetate esters and phthalate and stearate plasticizers

—Use as a stabilizing agent in metal cleaners, textile lubricants, oils, hydraulic fluids, and liquid household cleaners

The following methods are effective in controlling worker exposures to 2-butoxyethanol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-butoxyethanol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, kidneys, liver, respiratory system, and blood. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-butoxyethanol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin, kidney, liver, respiratory system, or blood diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-butoxyethanol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-butoxyethanol on the skin, kidney, liver, respiratory system, and blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although butoxy acetic acid (BAA), a metabolite of 2-butoxyethanol, can be detected in the urine of exposed individuals, excreted levels of butoxy acetic acid do not correlate with airborne concentrations of 2-butoxyethanol. Therefore, no biological monitoring test acceptable for routine use has yet been developed for

2-butoxyethanol. However, NIOSH has recommended guidelines for biological monitoring of BAA [NIOSH 1990].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne 2-butoxyethanol is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with methylene chloride/methanol (95:5) to extract the 2-butoxyethanol. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 to 0.02 mg per sample. This method is described in Method 1403 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984]. A similar method for sampling and analyzing 2-butoxyethanol is included in Method 83 of the *OSHA Analytical Methods Manual* [OSHA 1990].

PERSONAL HYGIENE

2-Butoxyethanol can be absorbed through the skin in toxic amounts. Therefore, if 2-butoxyethanol contacts the skin, workers should immediately flush the skin with large amounts of water and then wash with soap and water.

Clothing and shoes contaminated with 2-butoxyethanol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of 2-butoxyethanol, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles 2-butoxyethanol should thoroughly wash hands with soap and water before eating, using tobacco products, or using toilet facilities. Workers should not eat, drink, or use tobacco products in areas where 2-butoxyethanol is handled, processed, or stored.

STORAGE

2-Butoxyethanol should be stored in a cool, dry, dark, well-ventilated area in tightly sealed, resin-coated, stainless steel containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance should not be stored in aluminum containers. Electrical service in the storage area must be of explosionproof design. Containers of 2-butoxyethanol should be protected from physical damage and should be stored separately from strong oxidizers, strong caustics, heat, sparks, and open flame. Only nonsparking tools should be used to handle this substance. To prevent static sparks, all containers and equipment used to transfer 2-butoxyethanol must be bonded and grounded. Because containers that formerly contained 2-butoxyethanol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-butoxyethanol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres with maximally explosionproof ventilation.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the 2-butoxyethanol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2-Butoxyethanol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-butoxyethanol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-butoxyethanol emitted or released from their facility annually.

- ***Hazardous waste management requirements***

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although 2-butoxyethanol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- ***Conditions for respirator use***

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-butoxyethanol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with 2-butoxyethanol. Gloves, aprons, guantlets, boots, and other protective clothing should be worn as necessary. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber and Saranex® have been recommended for use against permeation by 2-butoxyethanol and may provide protection for periods greater than 8 hr. Natural rubber, polyvinyl alcohol, and polyvinyl chloride have demonstrated poor resistance to permeation by 2-butoxyethanol.

If 2-butoxyethanol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-butoxyethanol might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-butoxyethanol. Contact lenses should not be worn if the potential exists for 2-butoxyethanol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about n-butyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}O_2$

- **Structure**

$CH_3COO(CH_2)_3CH_3$

- **Synonyms**

n-Butyl acetate; butyl ethanoate; acetic acid, n-butyl ester; 1-butyl acetate

- **Identifiers**

1. CAS No.: 123-86-4
2. RTECS No.: AF7350000
3. DOT UN: 1123 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

n-Butyl acetate is a clear, colorless, flammable liquid with a fruity odor. The odor threshold is reported to be 0.7 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.2
2. Boiling point (at 760 mm Hg): 126°C (258°F)
3. Specific gravity (water = 1): 0.88 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butyl acetate): 4.0
5. Melting point: −77.9°C (−108.2°F)
6. Vapor pressure at 20°C (68°F): 10 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, ether, and most hydrocarbons
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires may result from contact of n-butyl acetate with potassium-tert-butoxide, nitrates, strong oxidizers, strong alkalies, and strong acids.
3. Hazardous decomposition products: Toxic gases and vapors (such as partial oxidation products, carbon dioxide, and carbon monoxide) may be released in a fire involving n-butyl acetate.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to n-butyl acetate.

1. Flash point: 22°C (72°F) (closed cup)
2. Autoignition temperature: 425°C (797°F)
3. Flammable limits in air (% by volume): Lower, 1.7; upper, 7.6
4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving n-butyl acetate. A stream of water should not be used to extinguish fires involving this substance because the water will scatter and spread the fire.

Fires involving n-butyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel.

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Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-butyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butyl acetate. Firefighters' protective clothing may not provide protection against permeation by n-butyl acetate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl acetate is 150 ppm (710 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 200 ppm (950 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 150 ppm (710 mg/m^3) as an 8-hr TWA and 200 ppm (950 mg/m^3) as a STEL [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butyl acetate a threshold limit value (TLV) of 150 ppm (713 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 200 ppm (950 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of sensory irritation associated with exposure to n-butyl acetate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to n-butyl acetate can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: n-Butyl acetate causes moderate to severe irritation of the eyes, skin, and upper respiratory tract in animals; at high concentrations, it can cause narcosis and death from respiratory failure. In rabbits, n-butyl acetate caused moderate skin irritation after 24 hr of exposure and severe eye irritation after instillation [NIOSH 1991]. Guinea pigs exposed to 3,300 ppm showed signs of eye irritation; exposure to 7,000 ppm for 11 hr caused narcosis [Proctor et al. 1988]. In rats, the oral LD_{50} is 14 g/kg, and the LC_{50} is 2,000 ppm for 4 hr [NIOSH 1991]. Nearly saturated vapor (10,000 ppm) was fatal to six rats following an 8-hr exposure. Mice exposed to n-butyl acetate at concentrations ranging from 3,100 to 4,200 ppm 6 hr/day for 6 days showed signs of fatigue, weight loss, and an increase in formed elements in the blood and in hemoglobin levels [NLM 1991]. When administered during pregnancy, n-butyl acetate was embryotoxic in mice and rats [NIOSH 1991; NLM 1991].

2. *Effects on Humans*: n-Butyl acetate is an irritant of the eyes, nose, respiratory tract, and skin in exposed workers. Volunteers exposed to n-butyl acetate at 200 ppm reported upper respiratory tract irritation; at 300 ppm, this irritation was reported to be severe [ACGIH 1991a]. Humans exposed to concentrations as high as 3,300 ppm experienced lacrimation and conjunctival redness [Grant 1986]. Vacuolar keratitis occurred in workers exposed to a mixture of butyl acetate and isobutyl alcohol. Hepatotoxicity has also been reported. Repeated skin contact with n-butyl acetate caused dermatitis in a pharmaceutical plant worker [NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to n-butyl acetate can cause contact irritation, headache, muscle weakness, giddiness, dizziness, ataxia, confusion, delirium, CNS and respiratory depression, coma, and death from respiratory failure.

2. *Chronic exposure*: Chronic exposure to n-butyl acetate can cause eye irritation and dryness, redness, scaling, and cracking of the skin.

• Emergency procedures

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-butyl acetate. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-butyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-butyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-butyl acetate and may result in worker exposures to this substance:

—Use of n-butyl acetate as a solvent and thinner for gums, oil, fats, waxes, pitch, lacquers, enamels, nitrocellulose, camphor, ethyl cellulose acetate, pyroxylin, chlorinated rubber, artificial leathers, ester-soluble dyes, airplane dopes, perfumes, natural gums, synthetic resins, and vinyl, polystyrene, and methacrylate plastics

—Application of nitrocellulose lacquers by spraying, brushing, or dipping and of surface coatings other than nitrocellulose lacquers, including paper coatings, lamp coatings, and airplane dope enamels

—Use of n-butyl acetate as a dehydrating agent

—Production of protective coatings in the automobile industry, flavorings, perfumes, safety glass, plastics, cosmetics, adhesives, shoe polishes, stain removers, photographic films, penicillin, and larvicides

The following methods are effective in controlling worker exposure to n-butyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to n-butyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-butyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-butyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-butyl acetate on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butyl acetate is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide or carbon disulfide/dimethylformamide to extract the n-butyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.02 mg per sample. This method is described in Method No. 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If n-butyl acetate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with n-butyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of n-butyl acetate, particularly its potential to be irritating to the skin.

A worker who handles n-butyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-butyl acetate or a solution containing n-butyl acetate is handled, processed, or stored.

STORAGE

n-Butyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance is an OSHA IB flammable liquid and must be handled accordingly. Containers of n-butyl acetate should be protected from physical damage and should be stored separately from potassium tert-butoxide, strong oxidizers, nitrates, strong alkalies, strong acids, explosives, heat, sparks, open flame, and materials that are readily impregnable by odor. Only nonsparking tools may be used to handle n-butyl acetate. To prevent static sparks, containers and equipment should be grounded and bonded for transfers. Because containers that formerly contained n-butyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-butyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the n-butyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulations resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for n-butyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Reponse Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-butyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of n-butyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with n-butyl acetate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by n-butyl acetate and have demonstrated protection for more than 4 but fewer than 8 hr: polyvinyl alcohol, Teflon®, and polyethylene/ethylene vinyl alcohol. Butyl rubber has demonstrated questionable protection from permeation. Natural rubber, neoprene, nitrile rubber, polyethylene, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by n-butyl acetate.

If n-butyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-butyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butyl acetate. Contact lenses should not be worn if the potential exists for n-butyl acetate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR sec-BUTYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about sec-butyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}O_2$

- **Structure**

$CH_3COOCH(CH_3)(C_2H_5)$

- **Synonyms**

Acetic acid, 1-methylpropyl ester; acetic acid, 2-butoxy ester; sec-butyl alcohol acetate; acetic acid, sec-butyl ester; 2-butyl acetate; 1-methylpropylacetate; 2-butanol acetate; acetic acid, secondary butyl ester

- **Identifiers**

1. CAS No.: 105-46-4
2. RTECS No.: AF7380000
3. DOT UN: 1123 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

sec-Butyl acetate is a flammable, colorless liquid with a mild fruity odor. The odor threshold is reported to be below 200 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.2
2. Boiling point (at 760 mm Hg): 112°C (233.6°F)
3. Specific gravity (water = 1): 0.88 at 16°C (60.8°F)
4. Vapor density (air = 1 at boiling point of sec-butyl acetate): 4.0
5. Melting point: −99°C (−146°F)
6. Vapor pressure at 20°C (68°F): 10 mm Hg
7. Solubility: Slightly soluble in water; miscible with common solvents
8. Evaporation rate (butyl acetate = 1): 2.0

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of sec-butyl acetate with nitrates, strong oxidizers, strong alkalies, or strong acids.
3. Hazardous decomposition products: Toxic gases and particulates (such as carbon monoxide, acrid smoke, and irritating fumes) may be released when sec-butyl acetate decomposes.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to sec-butyl acetate.

1. Flash point: 31°C (88°F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air (% by volume): Lower, 1.7; upper, 9.8

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

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4. Extinguishant: Use alcohol foam, carbon dioxide, dry chemical, or Halon® to fight fires involving sec-butyl acetate. Water may be ineffective for extinguishing fires, but it may be used to cool fire-exposed containers.

Fires involving sec-butyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of sec-butyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving sec-butyl acetate. Firefighters' protective clothing may not provide protection against permeation by sec-butyl acetate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for sec-butyl acetate is 200 ppm (950 mg/m^3) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 200 ppm (950 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned sec-butyl acetate a threshold limit value (TLV) of 200 ppm (950 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye and upper respiratory tract irritation associated with exposure to sec-butyl acetate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to sec-butyl acetate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: sec-Butyl acetate is an irritant of the eyes, skin, and upper respiratory tract. On the basis of effects seen in animals exposed to other acetates, it is likely that sec-butyl acetate will cause narcosis in animals exposed to high concentrations [Proctor et al. 1988].

2. *Effects on Humans*: sec-Butyl acetate is an irritant of the eyes and upper respiratory tract. Based on effects seen in humans exposed to chemically similar substances, sec-butyl acetate is likely to cause narcosis at high concentrations [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to sec-butyl acetate can cause redness and tearing of the eyes, runny nose, and sore throat. In contact with the skin, sec-butyl acetate may cause redness, defatting, and cracking. At high concentrations, workers may experience headache, fatigue, drowsiness, dizziness, or other symptoms of central nervous system depression and narcosis.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to sec-butyl acetate have been reported; however, prolonged exposure may increase the severity of the acute dermal effects noted above.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of sec-butyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of sec-butyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if sec-butyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of sec-butyl acetate may result in worker exposures to this substance:

—Use as a general solvent

—Use as a solvent for nitrocellulose, artificial leather, thinners, and nail enamels

The following methods are effective in controlling worker exposures to sec-butyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to sec-butyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to sec-butyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to sec-butyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of sec-butyl acetate on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for sec-butyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne sec-butyl acetate is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the sec-butyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.2 mg/sample. This method is described in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If sec-butyl acetate contacts skin, workers should wash the affected areas with soap and water.

Clothing and shoes contaminated with sec-butyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of sec-butyl acetate, particularly its potential for irritating the skin.

A worker who handles sec-butyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where sec-butyl acetate or a solution containing it is handled, processed, or stored.

STORAGE

sec-Butyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Electrical service in the storage area must meet requirements for an OSHA Class IB flammable liquid. To prevent static sparks, containers of sec-butyl acetate must be grounded and bonded. Containers also should be protected from physical damage and should be stored separately from direct sunlight, nitrates, strong oxidizers, strong alkalies, strong acids, heat, sparks, and open flames. Drums used to store sec-butyl acetate must be equipped with self-closing valves, pressure-vacuum bungs, and flame arresters. Only nonsparking tools may be used to transfer or handle sec-butyl acetate. Because containers that formerly contained sec-butyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving sec-butyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the sec-butyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

sec-Butyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.4] to notify the proper Federal, State, and local authorities.

The reportable quantity for sec-butyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of sec-butyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although sec-butyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of sec-butyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator*

Decision Logic [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with sec-butyl acetate. Gloves, aprons, and other protective clothing are recommended as necessary. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material is recommended for use against permeation by sec-butyl acetate: polyvinyl alcohol.

If sec-butyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which sec-butyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with sec-butyl acetate. Contact lenses should not be worn if the potential exists for sec-butyl acetate exposure.

REFERENCES CITED

ACGIH [1991a]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}O_2$

- **Structure**

$CH_3COOC(CH_3)_3$

- **Synonyms**

t-Butyl acetate; acetic acid, tert-butyl ester; acetic acid, 1,1-dimethyl ethyl ester; Texaco Lead Appreciator; TLA

- **Identifiers**

1. CAS No.: 540-88-5
2. RTECS No.: AF7400000
3. DOT UN: 1123 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

tert-Butyl acetate is a flammable, colorless liquid with a fruity odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.2
2. Boiling point (at 760 mm Hg): 97° to 98°C (206.6° to 208.4°F)
3. Specific gravity (water = 1): 0.87 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of tert-butyl acetate): 4.0
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water; soluble in alcohol and ether
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fire and explosions may result from contact of tert-butyl acetate with nitrates, strong oxidizers, strong alkalies, and strong acids.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving tert-butyl acetate.
4. Special precautions: tert-Butyl acetate may soften or dissolve plastics.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to tert-butyl acetate; however, other sources rate this substance's fire hazard potential as severe.

1. Flash point: Between 16.6° and 22°C (62° and 72°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air (% by volume): Lower, 1.5; upper, data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use alcohol foam, carbon dioxide, dry chemical, water spray, or Halon® to fight fires involving tert-butyl acetate.

Fires involving tert-butyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of tert-butyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing, including a self-contained breathing apparatus, when fighting fires involving tert-butyl acetate. Firefighters' protective clothing may not provide protection against permeation by tert-butyl acetate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl acetate is 200 ppm (950 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 200 ppm (950 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl acetate a threshold limit value (TLV) of 200 ppm (950 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991a].

• Rationale for limits

The limits are based on the risk of eye and respiratory tract irritation associated with exposure to tert-butyl acetate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to tert-butyl acetate can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: tert-Butyl acetate has not been tested for toxicity in animals. However, by analogy with the effects of other acetate esters, tert-butyl acetate is likely to cause eye, nose, and skin irritation and, at high concentrations, narcosis [Proctor et al. 1988].

2. *Effects on Humans*: Exposure to tert-butyl acetate causes eye, skin, and respiratory irritation in workers. By analogy with the effects of similar esters, tert-butyl acetate is likely to cause narcosis at high concentrations [ACGIH 1991a].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to tert-butyl acetate can cause itchy or inflamed eyes and irritation of the nose and upper respiratory tract. Exposure to high concentrations of tert-butyl acetate may cause headache, drowsiness, and other narcotic effects.

2. *Chronic exposure*: No chronic effects of exposure to tert-butyl acetate have been reported; however, prolonged exposure may increase the severity of the acute dermal effects noted above.

• Emergency procedures

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of tert-butyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if tert-butyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of tert-butyl acetate may result in worker exposures to this substance:

—Use as a solvent

—Use as an additive to improve the antiknock properties of motor fuels

The following methods are effective in controlling worker exposures to tert-butyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to tert-butyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl acetate on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for tert-butyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne tert-butyl acetate is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.02 mg per sample. This method is described in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If tert-butyl acetate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with tert-butyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of tert-butyl acetate, particularly its potential to be irritating to the eyes and skin.

A worker who handles tert-butyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities. Workers should not eat, drink, or use tobacco products in areas where tert-butyl acetate is handled, processed, or stored.

STORAGE

tert-Butyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of tert-butyl acetate should be protected from physical damage and should be stored separately from nitrates, strong oxidizers, strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained tert-butyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a leak involving tert-butyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Use water spray to reduce vapors, but be aware that the spray may not prevent ignition in closed spaces.

6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

tert-Butyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

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A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for tert-butyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of tert-butyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although tert-butyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of tert-butyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with tert-butyl acetate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to permeation by tert-butyl acetate; however, the following materials have been tested against permeation by a chemically similar substance (n-butyl acetate) and have demonstrated protection for more than 4 but fewer than 8 hr: polyvinyl alcohol, polyethylene/ethylene vinyl alcohol, and Teflon®. Natural rubber, neoprene, nitrile rubber, polyethylene, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by n-butyl acetate. Since specific test data are not available for tert-butyl acetate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to tert-butyl acetate.

If tert-butyl acetate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl acetate. Contact lenses should not be worn if the potential exists for tert-butyl acetate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BUTYL ACRYLATE

INTRODUCTION

This guideline summarizes pertinent information about butyl acrylate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{12}O_2$

- **Structure**

$CH_2{=}CHCOOC_4H_9$

- **Synonyms**

2-Propenoic acid, butyl ester; acrylic acid, butyl ester; acrylic acid, n-butyl ester; butyl 2-propenoate

- **Identifiers**

1. CAS No.: 141-32-2
2. RTECS No.: UD3150000
3. DOT UN: 2348 26 (for the inhibited form)
4. DOT label: Flammable Liquid

- **Appearance and odor**

Butyl acrylate is a flammable, clear, colorless liquid with a sharp, fragrant, characteristic odor. The odor threshold is reported to be 0.1 part per billion (ppb) parts of air. Butyl acrylate is highly reactive and can undergo spontaneous polymerization. To prevent premature polymerization, the commercially available product often contains an inhibitor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 128.17
2. Boiling point (760 mm Hg): 145°C (293°F) (polymerizes)
3. Specific gravity (water = 1): 0.9 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of butyl acrylate): 4.4
5. Melting point: −64°C (−83.2°F)
6. Vapor pressure at 20°C (68°F): 4 mm Hg
7. Solubility: Very slightly soluble in water; soluble in alcohol, ether, and acetone.
8. Evaporation rate (butyl acetate = 1): 0.42

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame (heat may cause an explosive polymerization reaction)
2. Incompatibilities: Hazardous polymerization may result from contact of butyl acrylate with peroxides, sunlight, or other catalysts. Butyl acrylate is incompatible with strong acids, strong alkalies, amines, halogens, hydrogen compounds, and oxidizers.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving butyl acrylate.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to butyl acrylate.

1. Flash point: 49°C (120°F) (open cup)
2. Autoignition temperature: 293°C (559°F)
3. Flammable limits in air (% by volume): Lower, 1.4; upper, 9.9

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4. Extinguishant: Use dry chemical, foam, or carbon dioxide to fight fires involving butyl acrylate. Water may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving butyl acrylate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of butyl acrylate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving butyl acrylate. Firefighters' protective clothing may not provide protection against permeation by butyl acrylate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for butyl acrylate is 10 ppm (55 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (55 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned butyl acrylate a threshold limit value (TLV) of 10 ppm (52 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye and skin irritation associated with exposure to butyl acrylate and on its toxicological similarity to methyl acrylate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to butyl acrylate can occur through inhalation, eye or skin contact, and absorption through the skin.

• Summary of toxicology

1. *Effects on Animals*: Butyl acrylate is an irritant of the eyes, skin, and respiratory tract in animals. Instillation of this substance into the eyes of rabbits also caused mild to moderate irritation [NIOSH 1991]. Corneal necrosis occurred when ocular washing was not performed [ACGIH 1991a]. When applied to the skin of rabbits for 24 hr, 10 mg butyl acrylate caused mild irritation. Butyl acrylate is a sensitizer in guinea pigs, and sensitized animals showed cross-sensitization reactions to other monoacrylates [IARC 1986]. The dermal LD_{50} for rabbits has ranged from 1,800 to 3,000 mg/kg [Carpenter et al. 1974; Smyth et al. 1951]. The maximum duration that all rats survived exposure to inhalation of saturated vapors (7,050 ppm) was 30 min [ACGIH 1991a; Smyth et al. 1951]. The 2-hr LC_{50} is 1,345 ppm for mice and 6,035 ppm for rats [Izmerov et al. 1982]. The 4-hr LC_{50} in rats is 2,730 ppm [NIOSH 1991]. These animals exhibited signs of eye and respiratory tract irritation (e.g., corneal necrosis and labored breathing) [ACGIH 1991a; Proctor et al. 1988]. Wide variations are reported in the oral LD_{50} for rats: 900 mg/kg [Izmerov et al. 1982]; 3,730 mg/kg [Smyth et al. 1951]; and 8,050 mg/kg [Carpenter et al. 1974]. The oral LD_{50} in mice has ranged from 5,400 to 7,500 mg/kg [IARC 1986]. Rats were exposed for 6 hr/day to 25, 135, or 250 ppm on days 6 to 15 after mating. Maternal toxicity and embryo lethality occurred at the two highest doses, but exposure to 25 ppm caused no observable effects. However, terata were not induced by any concentration of butyl acrylate [Proctor et al. 1988]. The International Agency for Research on Cancer (IARC) found no evidence of mutagenic potential in the in vivo or in vitro data reviewed [IARC 1986]. In a dermal carcinogenesis study, 1% butyl acrylate in acetone was applied three times weekly to the skin of mice over their lifetimes; no site-of-application tumors occurred in these animals [Proctor et al. 1988]. In a 2-year inhalation study, Sprague-Dawley rats were exposed to butyl acrylate concentrations ranging from 15 to 135 ppm. Exposures were for 6 hr/day, 5 days/week for 24 months followed by a 6-month recovery period. No tumors were induced by butyl acrylate after either the treatment or recovery periods [IARC 1986]. IARC has concluded that there is inadequate evidence of the carcinogenicity of butyl acrylate in animals [IARC 1986].

2. *Effects on Humans*: Butyl acrylate is an irritant of the eyes and skin as well as the mucous membranes of the nose, throat, and respiratory tract in humans [Gosselin et al. 1984]. Allergic contact dermatitis attributed to butyl acrylate has

been reported in dentists, dental technicians, paint stock room clerks, and other occupationally exposed individuals [Kanerva et al. 1988; Proctor et al. 1988]. Fourteen of 33 workers exposed to 50 mg/m^3 (approximately 10 ppm) for an average of 5 years reported experiencing nervous system and behavioral symptoms, but these were not confirmed by electroencephalography [IARC 1986]. IARC classified butyl acrylate as a Group 3 material (not classifiable as to its carcinogenicity to humans) [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to butyl acrylate vapor can cause redness, tearing, and irritation of the eyes, runny nose, scratchy throat, difficult breathing, and redness and cracking of the skin.

2. *Chronic exposure*: Repeated contact of the skin with this substance may cause skin sensitization in some individuals, with redness, swelling, itching, and oozing of the affected areas. Nervous system and behavioral effects are also possible.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or [illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of butyl acrylate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of butyl acrylate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if butyl acrylate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve butyl acrylate and may result in worker exposures to this substance:

—Manufacture of polymers and resins for leather finishes, paint formulations, and textiles

—Organic synthesis of polymers and copolymers for solvent coatings, paper, adhesives, binders, sealants, and emulsifiers

The following methods are effective in controlling worker exposures to butyl acrylate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to butyl acrylate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to butyl acrylate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies or other findings consistent with skin or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to butyl acrylate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of butyl acrylate on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for butyl acrylate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne butyl acrylate is determined by using two XAD-2 tubes in series (80/50-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 3 liters is collected. The sample is then treated with carbon disulfide to extract the butyl acrylate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If butyl acrylate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with butyl acrylate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of butyl acrylate, particularly its potential for causing skin irritation and sensitization.

A worker who handles butyl acrylate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where butyl acrylate or a solution containing butyl acrylate is handled, processed, or stored.

STORAGE

Butyl acrylate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The inhibitor concentration in containers of this substance should be checked at regular intervals and inhibitor should be added as needed. Butyl acrylate should be stored at temperatures below 38°C (100°F). Containers of butyl acrylate should be protected from physical damage and should be stored separately from peroxides, strong acids, strong alkalies, amines, halogens, hydrogen compounds, oxidizers, sunlight, heat, sparks, and open flame. Because containers that formerly contained butyl acrylate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving butyl acrylate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the butyl acrylate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Butyl acrylate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of butyl acrylate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of butyl acrylate per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of butyl acrylate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although butyl acrylate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of butyl acrylate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with butyl acrylate; impervious gloves are recommended. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been tested against permeation by butyl acrylate and has demonstrated good-to-excellent resistance for more than 4 but fewer than 8 hr. Butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by butyl acrylate.

If butyl acrylate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which butyl acrylate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with butyl acrylate. Contact lenses should not be worn if the potential exists for butyl acrylate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about n-butyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{10}O$

- **Structure**

$CH_3CH_2CH_2CH_2OH$

- **Synonyms**

1-Butanol, n-butanol, n-propyl carbinol, NBA, butyl hydroxide, butyric alcohol, normal primary butyl alcohol, methylal propane, propylmethanal, 1-hydroxybutane

- **Identifiers**

1. CAS No.: 71-36-3
2. RTECS No.: EO1400000
3. DOT UN: 1120 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

n-Butyl alcohol is a flammable, colorless liquid with a mild, wine-like odor. The odor threshold is reported to be between 0.12 and 11.0 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (at 760 mm Hg): 117° to 118°C (243° to 244°F)
3. Specific gravity (water = 1): 0.81 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butyl alcohol): 2.6
5. Melting point: −90°C (−130°F)
6. Vapor pressure at 20°C (68°F): 6 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, ether, and many other organic solvents
8. Evaporation rate (butyl acetate = 1): 0.46

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of n-butyl alcohol with strong oxidizers, strong mineral acids, alkali metals, or halogens.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving n-butyl alcohol.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to n-butyl alcohol.

1. Flash point: 37°C (98°F) (closed cup)
2. Autoignition temperature: 343°C (650°F)
3. Flammable limits in air (% by volume): Lower, 1.4; upper, 11.3
4. Extinguishant: Use carbon dioxide, dry chemical, or alcohol foam to fight fires involving n-butyl alcohol. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving n-butyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area

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and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and should ventilate closed spaces before entering. Containers of n-butyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butyl alcohol. Firefighters' protective clothing may not provide protection against permeation by n-butyl alcohol.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl alcohol is 50 ppm (150 mg/m^3) as a ceiling limit. A worker's exposure to n-butyl alcohol shall at no time exceed this limit. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (150 mg/m^3) as a ceiling limit with a "Skin" notation [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butyl alcohol a ceiling limit of 50 ppm (152 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH has also assigned n-butyl alcohol a "Skin" notation [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of possible vestibular and auditory nerve injury as well as headaches and irritation associated with exposure to n-butyl alcohol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to n-butyl alcohol can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: n-Butyl alcohol is an irritant of the eyes, skin, and respiratory tract in animals; at high concentrations, exposure causes narcosis. In rabbits, n-butyl alcohol causes moderate skin irritation upon contact and severe corneal irritation when instilled into the eyes [NIOSH 1991]. The dermal LD_{50} in rabbits ranges from 3,400 to 5,300 mg/kg [NIOSH 1991; IPCS 1987]. The oral LD_{50}s in rats ranges from 700 to 2,100 mg/kg [IPCS 1987]. The 4-hr LC_{50} for rats is 8,000 ppm [NIOSH 1991]. Death also occurred in two of six female rats that inhaled 9,000 ppm for 7 hr. Half of another group of female rats that inhaled 8,000 ppm for 7 hr also developed narcosis. However, females that inhaled 6,000 ppm were asymptomatic throughout and after the 7-hr exposure period [Nelson et al. 1989]. Mice exposed to 3,300 ppm for 7 hr showed no effects, and 6,600 ppm caused giddiness within 1 hr, prostration within 2 hr, and loss of reflexes after 3 hr, with respiratory failure, deep narcosis, and death in some animals [Clayton and Clayton 1981]. Guinea pigs exposed to 100 ppm for 4 hr/day, 6 days/week for a total of 64 exposures showed lymphocytopenia and erythropenia; at autopsy, lung hemorrhage and degeneration of the liver and kidneys were seen [Clayton and Clayton 1981]. Groups of female rats were exposed to 8,000, 6,000, 3,500, or 0 ppm sec-butyl alcohol for 7 hr/day on gestation days 1 through 19. Absorbed daily doses for each of these exposure concentrations were theorized to be 800, 600, 350, or 0 mg/kg, respectively. Two of 18 dams exposed at 8,000 ppm died. Fetal weights were slightly depressed at 8,000 and 6,000 ppm. A slight but statistically significant increase in skeletal malformations (primarily rudimentary cervical ribs) occurred in pups obtained from 8,000-ppm-exposed dams who exhibited the presence of maternal toxicity (reduced weight gain and food consumption) [Nelson et al. 1989]. n-Butyl alcohol was not mutagenic when tested with in vitro assays [IPCS 1987]. Two long-term n-butyl alcohol tests have been performed but were considered inadequate for assessment of carcinogenic activity [IPCS 1987].

2. *Effects on Humans*: n-Butyl alcohol causes eye, skin, and upper respiratory tract irritation in exposed workers. Volunteers reported mild irritation of the eyes, nose, and throat when exposed to 25 ppm. Unacclimatized subjects exposed to 50 ppm experienced pronounced throat irritation, and several of them developed delayed onset headaches [ACGIH 1991a]. Workers chronically exposed to 100 ppm rarely complained of eye irritation, where as previous exposures to 200 ppm or more caused corneal inflammation, an ocular burning sensation, blurred vision, lacrimation, and photophobia [ACGIH 1991a]. Repeated or prolonged contact of n-butyl alcohol with the skin causes defatting and contact dermatitis, and this substance can be absorbed through the skin in toxic amounts [Proctor et al. 1988].

Vertigo and auditory nerve and vestibular system damage have been reported in Mexican and French workers exposed both to n-butyl alcohol and workplace noise, but the relative contribution of the alcohol to these effects has not been determined [ACGIH 1991a; Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-butyl alcohol can cause redness and tearing of the eyes, scratchy throat, itching and redness of the skin, headache, ataxia, prostration, deep narcosis, respiratory failure, and death.

2. *Chronic exposure*: Chronic exposure to n-butyl alcohol can cause photophobia, blurred vision, corneal vacuoles, and defatting and itching of the skin. Chronic exposure to n-butyl alcohol can cause vertigo and may increase the extent of hearing loss among workers exposed to both noise and n-butyl alcohol.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-butyl alcohol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-butyl alcohol are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-butyl alcohol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-butyl alcohol and may result in worker exposures to this substance:

—Formulation of nitrocellulose lacquers, latexes, rayon detergents, esters, other butyl compounds, and plastic and rubber cements

—Use of n-butyl alcohol as a solvent or diluent in brake fluids, perfumes, detergents, adhesives, denatured alcohol, surface coatings, fats, waxes, natural and synthetic paints, resins, shellac, varnishes, gums, vegetable oils, dyes, camphor, and alkaloids

—Manufacture of artificial leather, safety glass, derivatives of butyl alcohol (including chemicals, herbicides, flotation agents, and urea and melamine formaldehyde resins), pharmaceuticals (including antibiotics, hormones, and vitamins), and bactericides for veterinary use

—Use of n-butyl alcohol during photographic processing operations and in the manufacture of photographic film

—Use of n-butyl alcohol in textile making as a swelling agent, dye ingredient, and waterproofing agent

—Use of n-butyl alcohol as an azeotropic dehydration agent and blending agent in laboratory analysis and in microscopy to prepare paraffin imbedding materials

The following methods are effective in controlling worker exposures to n-butyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to n-butyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-butyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-butyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-butyl alcohol on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butyl alcohol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butyl alcohol is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh). To determine TWA concentrations, samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected; to determine ceiling limit concentrations, samples are collected for a minimum of

5 min. The sample is desorbed with carbon disulfide/isopropanol (99:1) or carbon disulfide/dimethylformamide (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method No. 1401 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If n-butyl alcohol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with n-butyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of n-butyl alcohol, particularly its potential to be absorbed through the skin.

A worker who handles n-butyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-butyl alcohol or a solution containing n-butyl alcohol is handled, processed, or stored.

STORAGE

n-Butyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical service in the storage area must meet OSHA requirements for Class IC flammable liquids [29 CFR 1910.106]. Small amounts of n-butyl alcohol should be stored in metal safety cans in OSHA-approved safety cabinets or storerooms. Containers of n-butyl alcohol should be protected from physical damage and should be stored separately from oxidizing agents, strong mineral acids, alkali metals, halogens, explosives, organic peroxides, radioactive materials, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle n-butyl alcohol. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained n-butyl alcohol may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-butyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the n-butyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butyl alcohol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for n-butyl alcohol is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of n-butyl alcohol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. n-Butyl alcohol is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U031. This chemical is approved for land disposal as long as the concentration in the waste or treatment residual does not exceed 2.6 mg/kg. n-Butyl alcohol also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with n-butyl alcohol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been recommended for use against permeation by n-butyl alcohol and may provide protection for periods greater than 8 hr. Materials that may withstand permeation for more than 4 but fewer than 8 hr are butyl rubber, neoprene, nitrile rubber, polyethylene, and polyethylene/ethylene vinyl alcohol. Polyvinyl alcohol and polyvinyl chloride provide questionable protection from permeation, and natural rubber has demonstrated poor resistance to permeation by n-butyl alcohol.

If n-butyl alcohol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-butyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butyl alcohol. Contact lenses should not be worn if the potential exists for n-butyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR sec-BUTYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about sec-butyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{10}O$

- **Structure**

$CH_3CH_2CH(OH)CH_3$

- **Synonyms**

2-Butanol, sec-butanol, 2-butyl alcohol, methyl ethyl carbinol, butylene hydrate, 2-hydroxybutane

- **Identifiers**

1. CAS No.: 78-92-2
2. RTECS No.: EO1750000
3. DOT UN: 1120 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

sec-Butyl alcohol is a colorless, flammable, volatile liquid with a strong, winelike odor. The odor threshold is reported to be between 0.4 and 2.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): 99.5°C (211.1°F)
3. Specific gravity (water = 1): 0.81 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of sec-butyl alcohol): 2.55
5. Melting point: −115°C (−175°F)
6. Vapor pressure at 20°C (68°F): 12 mm Hg
7. Solubility: Moderately soluble in water; miscible with alcohol, ether, and most organic solvents
8. Evaporation rate (butyl acetate = 1): 1.3

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. sec-Butyl alcohol auto-oxidizes to form an explosive peroxide.
2. Incompatibilities: Fires and explosions may result from contact of sec-butyl alcohol with strong oxidizers, organic peroxides, or perchloric or permonosulfuric acid. sec-Butyl alcohol ignites on contact with chromium trioxide.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released when sec-butyl alcohol decomposes.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (dangerous fire hazard) to sec-butyl alcohol.

1. Flash point: 24°C (75°F)
2. Autoignition temperature: 405°C (761°F)

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air at 100°C (212°F) (% by volume): Lower, 1.7; upper, 9.8

4. Extinguishant: Use alcohol foam, carbon dioxide, or dry chemical to fight fires involving sec-butyl alcohol. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving sec-butyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Vapors may travel to a source of ignition and flash back. Vapor explosion hazards may occur indoors, outdoors, or in sewers. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of sec-butyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving sec-butyl alcohol. Firefighters' protective clothing may not provide protection against permeation by sec-butyl alcohol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for sec-butyl alcohol is 100 ppm (305 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 100 ppm (305 mg/m^3) as an 8-hr TWA and 150 ppm (455 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned sec-butyl alcohol a threshold limit value (TLV) of 100 ppm (303 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risks of narcosis and irritation associated with exposure to sec-butyl alcohol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to sec-butyl alcohol can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: In animals, sec-butyl alcohol is an eye irritant and, at high concentrations, a narcotic. Although it is not an irritant when in contact with rabbit skin, it can induce severe corneal injury when directly instilled into the eyes of rabbits [Grant 1986; NLM 1991]. Five of six rats died following an exposure of 16,000 ppm for 4 hr [Clayton and Clayton 1981]. Death also occurred in all five female rats that inhaled 10,000 ppm for 7 hr. Another group of female rats exposed to 7,000 ppm for 7 hr did not die and had not completely recovered from the induced narcosis on the day following exposure. Female rats exposed to 5,000 ppm also had impaired motor activity and developed narcosis [Nelson et al. 1989]. Inhalation of 10,670 ppm for 225 min or 16,000 ppm for 160 min was fatal to exposed mice [Clayton and Clayton 1981]. Mice that inhaled exposures ranging from 3,300 ppm for 5 hr to 19,800 ppm for 40 min developed restlessness, ataxia, prostration, and narcosis but did not die [NLM 1991]. Mice were unaffected by exposure to 1,650 ppm for 7 hr [ACGIH 1991a]. The oral LD_{50} in the rat is 6.5 g/kg [NIOSH 1991]. Mice exposed repeatedly to a sec-butyl alcohol concentration of 5,330 ppm for a total of 117 hr developed narcosis but survived the exposure [Clayton and Clayton 1981]. Groups of female rats were exposed to 7,000, 5,000, 3,500, or 0 ppm sec-butyl alcohol for 7 hr/day on gestation days 1 through 19. Absorbed daily doses for each of these respective exposure concentrations were theorized to be 700, 500, 350, or 0 mg/kg. No deaths occurred, but weight gain and food consumption were depressed for dams at each sec-butyl alcohol exposure concentration. The number of live fetuses was significantly reduced, resorptions increased, and the fetal weights were slightly depressed at 7,000 and 5,000 ppm [Nelson et al. 1989]. In two mutagenicity assays, *Schizosaccharomyces pombe* (yeast) and V-79 Chinese hamster cells, sec-butyl alcohol was nonmutagenic [IPCS 1987].

2. *Effects on Humans*: sec-Butyl alcohol has a defatting effect on the skin [Proctor et al. 1988]. Workers repeatedly exposed to 100 ppm have not developed signs or symptoms

of toxicity or irritation [Proctor et al. 1988]. However, two patients who had become sensitized to primary alcohols tested positive when challenged with sec-butyl alcohol [NLM 1991]. Excessive exposure may result in headache, dizziness, drowsiness, and narcosis [IPCS 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to sec-butyl alcohol can cause eye, nose, and throat irritation, with redness and tearing of the eyes, runny nose, defatting of skin, and cough. Exposure to high concentrations of sec-butyl alcohol is likely to cause headache, fatigue, nausea, dizziness, and narcosis.

2. *Chronic exposure*: Chronic exposure to sec-butyl alcohol can cause dermatitis in chronically exposed workers and may cause intense dermal sensitization in some exposed individuals.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of sec-butyl alcohol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of sec-butyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if sec-butyl alcohol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve sec-butyl alcohol and may result in worker exposures to this substance:

—Use of sec-butyl alcohol as an adhesive in the manufacture of plywood and as a chemical intermediate in the production of methyl ethyl ketone, sec-butyl acetate, and xanthate

—Use of sec-butyl alcohol as a solvent for natural resins, linseed oil, castor oil, lacquer, paint removers, and adhesives

—Manufacture of flotation agents, hydraulic fluids, flavors, perfumes, dyestuffs, wetting agents, paint removers, industrial cleaners, and polishes

—Use of sec-butyl alcohol as a dehydrating agent, an antifoaming agent, and an ingredient in dewaxing paraffin

The following methods are effective in controlling worker exposures to sec-butyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. *Industrial ventilation—a manual of recommended practice*. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to sec-butyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to sec-butyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, and respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to sec-butyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of sec-butyl alcohol on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for sec-butyl alcohol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne sec-butyl alcohol is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The samples are desorbed either with carbon disulfide/isopropanol (99:1) or carbon disulfide/dimethylformamide (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg/sample. This method is described in Method No. 1401 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If sec-butyl alcohol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with sec-butyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of sec-butyl alcohol, particularly its potential to be irritating to the eyes and skin.

A worker who handles sec-butyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where sec-butyl alcohol is handled, processed, or stored.

STORAGE

sec-Butyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet OSHA requirements for Class IC flammable liquids. Drums must be equipped with self-closing valves, pressure-vacuum bungs, and flame arrestors. Containers of sec-butyl alcohol should be protected from physical damage and should be kept separate from oxidizing agents, explosives, heat, sparks, and open flame. Small amounts of this substance may be stored in metal safety cans in OSHA-approved safety cabinets or storage rooms. Only nonsparking tools may be used to handle sec-butyl alcohol. To prevent static sparks, containers should be grounded and bonded during transfers. Because containers that formerly contained sec-butyl alcohol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving sec-butyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the sec-butyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

sec-Butyl alcohol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of sec-butyl alcohol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of sec-butyl alcohol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of sec-butyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although sec-butyl alcohol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of sec-butyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with sec-butyl alcohol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by sec-butyl alcohol and may withstand permeation for more than 4 but fewer than 8 hr: butyl rubber and polyethylene/ethylene vinyl alcohol.

If sec-butyl alcohol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which sec-butyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with sec-butyl alcohol. Contact lenses should not be worn if the potential exists for sec-butyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{10}O$

- **Structure**

$(CH_3)_3COH$

- **Synonyms**

tert-Butanol; 2-methyl-2-propanol; TBA; t-butyl hydroxide; 1,1-dimethylethanol; trimethylmethanol; trimethylcarbinol

- **Identifiers**

1. CAS No.: 75-65-0
2. RTECS No.: EO1925000
3. DOT UN: 1120 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

tert-Butyl alcohol is a colorless, crystalline solid or a volatile liquid (above 77°F) that has a camphorlike odor. The odor threshold is reported to be below 0.8 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): 82.4°C (180°F)
3. Specific gravity (water = 1): 0.79 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of tert-butyl alcohol): 2.55
5. Melting point: 25.6°C (78.1°F)
6. Vapor pressure at 20°C (68°F): 31 mm Hg
7. Solubility: Soluble in water; miscible with alcohol and ether
8. Evaporation rate (butyl acetate = 1): 1.05

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact with oxidizing agents, strong mineral acids, or strong hydrochloric acid.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide or isobutylene) may be released when tert-butyl alcohol decomposes in contact with strong mineral acids.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (dangerous fire hazard) to tert-butyl alcohol.

1. Flash point: 11°C (52°F) (closed cup)
2. Autoignition temperature: 478°C (892°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air (% by volume): Lower, 2.4; upper, 8.0

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol foam, or water fog to fight fires involving tert-butyl alcohol. Blanket the fire to smother it. Water may be ineffective in extinguishing the fire, but a water spray may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to dilute spills to a nonflammable mixture.

Fires involving tert-butyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapors may travel to a source of ignition and then flash back. Vapor explosions may occur indoors, outdoors, or in sewers. Containers of tert-butyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving tert-butyl alcohol. Firefighters' protective clothing may not provide protection against permeation by tert-butyl alcohol.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl alcohol is 100 ppm (300 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 150 ppm (450 mg/m^3) as a 15-min short-term exposure limit (STEL). A STEL is a 15-min TWA concentration that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 100 ppm (300 mg/m^3) as an 8-hr TWA and 150 ppm (450 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl alcohol a threshold limit value (TLV) of 100 ppm (303 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek with a STEL of 150 ppm (455 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of narcotic effects associated with exposure to tert-butyl alcohol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to tert-butyl alcohol can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: tert-Butyl alcohol causes narcosis in animals exposed to high concentrations. The oral LD_{50} in rats is 3,500 mg/kg [NIOSH 1991]. Prolonged contact of tert-butyl alcohol with the skin of rabbits caused no irritation [Clayton and Clayton 1981]. When six female rats were exposed to 10,000 ppm for 7 hr, all developed severe narcosis and five died. Female rats in another group that inhaled 5,000 ppm for 7 hr also developed ataxia and narcosis but did not die. A 2,000-ppm exposure resulted in ataxia alone [Nelson et al. 1989]. Compared with other butyl alcohols, tert-butyl alcohol is reported to have a stronger narcotic effect on mice and rats [ACGIH 1991a; Nelson et al. 1989]. Rats given nontoxic oral doses of tert-butyl alcohol (0.0163 mol/kg) showed a marked decline in motor performance test scores; tert-butyl alcohol caused a narcotic effect estimated to be 4.8 times greater than that of ethanol [Clayton and Clayton 1981]. In a teratology study, groups of pregnant rats were exposed to 5,000, 3,500, 2,000, or 0 ppm tert-butyl alcohol for 7 hr/day during gestation days 1 through 19. Absorbed daily doses for each of these respective exposure levels were theorized to be 500, 350, 200, or 0 mg/kg. Depressed maternal weight gain and food consumption were induced only at 5,000 ppm. Fetal weights were statistically depressed in a dose-related fashion for all three alcohol exposures, and skeletal variations were statistically increased only at 5,000 and 3,500 ppm [Nelson et al. 1989]. The effect of prenatal ethanol or tert-butyl alcohol exposure on postnatal development was studied in mice. Daily ingestion of a diet deriving 1% of its calories from tert-butyl alcohol reduced maternal weight gain and food consumption and increased the number of stillborn pups. The authors concluded that this compound was five times more potent than ethanol in producing developmental delay in postnatal physiologic and psychomotor performance [Daniel and Evans 1982]. Ethanol and tert-butyl alcohol exposures were also compared for their potential to induce microcephaly in neonatal rats. Using an artificial rearing technique and exposures during developmental

days 4 through 7, microcephaly was induced by both of these alcohols [Grant and Sampson 1982]. This compound has been tested in a wide variety of mutagenicity assays, all of which confirm it to be a nonmutagen [IPCS 1987]. The National Toxicology Program (NTP) has completed one carcinogenicity study in mice and rats administered tert-butyl alcohol in drinking water. However, they judged this study to be inadequate for publication. The NTP has also completed subchronic tert-butyl alcohol inhalation studies in mice and rats and intends to conduct a set of inhalation carcinogenicity studies in these species [NTP 1992].

2. *Effects on Humans*: tert-Butyl alcohol causes eye and mucous membrane irritation. In contact with the skin of humans, tert-butyl alcohol caused slight redness, hyperemia, and irritation; prolonged skin contact may cause contact dermatitis [Clayton and Clayton 1981; NLM 1991]. A positive patch test was found in an individual who had an allergic skin reaction to a skin screen that contained tert-butyl alcohol [ACGIH 1991a]. Exposure to excessive (not further specified) concentrations caused eye, nose, and throat irritation, headache, nausea, fatigue, dizziness, and narcosis in humans [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to tert-butyl alcohol can cause irritation and redness of the eyes, runny nose, scratchy throat, headache, nausea, fatigue, dizziness, and redness and drying of the skin.

2. *Chronic exposure*: Chronic exposure to tert-butyl alcohol can cause defatting of the skin and dermatitis.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl alcohol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of tert-butyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if tert-butyl alcohol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve tert-butyl alcohol and may result in worker exposures to this substance:

—Use of tert-butyl alcohol as a solvent for paints, lacquers, varnishes, natural and synthetic resins, gums, vegetable oils, dyes, camphor, and alkaloids, and as an octane booster in unleaded gasoline

—Manufacture of artificial leather, safety glass, rubber and plastic cements, shellac, raincoats, photographic films, flotation agents, fruit essences, perfumes, cellulose esters, lacquers, paint removers, and plastics

—Use of tert-butyl alcohol as a denaturant for alcohol and as a chemical intermediate in the manufacture of methyl methacrylate and pharmaceuticals

The following methods are effective in controlling worker exposures to tert-butyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

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2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to tert-butyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl alcohol on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for tert-butyl alcohol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne tert-butyl alcohol is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected (for TWA monitoring) or a maximum air volume of 3 liters is collected (for STEL monitoring). The sample is then desorbed with carbon disulfide/2-butanol (99:1) or with carbon disulfide/dimethylformamide (99:1) to extract the tert-butyl alcohol. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in the OSHA Computerized Information System [OSHA 1990] and in Method 1400 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If tert-butyl alcohol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with tert-butyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of tert-butyl alcohol, particularly its potential for irritating the skin.

A worker who handles tert-butyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where tert-butyl alcohol is handled, processed, or stored.

STORAGE

tert-Butyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of tert-butyl alcohol should be protected from physical damage and should be stored separately from strong oxidizers, strong mineral acids, strong hydrochloric acid, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure-vacuum bungs, and flame arrestors. Only nonsparking tools and equipment may be used to handle tert-butyl alcohol. To prevent static sparks, containers of tert-butyl alcohol should be grounded and bonded for transfers. Because containers that formerly contained tert-butyl alcohol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving tert-butyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors, but be aware that the spray may not prevent ignition in closed spaces.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

tert-Butyl alcohol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of tert-butyl alcohol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of tert-butyl alcohol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of tert-butyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although tert-butyl alcohol is not specifically listed as a hazardous waste under the Resource Conservation and

Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with tert-butyl alcohol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber has been tested against permeation by tert-butyl alcohol and has demonstrated good-to-excellent resistance for periods greater than 8 hr. Polyethylene ethylene/vinyl alcohol may withstand permeation for more than 4 but fewer than 8 hr.

If tert-butyl alcohol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl alcohol. Contact lenses should not be worn if the potential exists for tert-butyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BUTYLAMINE

INTRODUCTION

This guideline summarizes pertinent information about butylamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{11}N$

- **Structure**

$CH_3CH_2CH_2CH_2NH_2$

- **Synonyms**

1-Butylamine, n-butylamine, 1-aminobutane, 1-butanamine, Norvalamine, mono-n-butylamine

- **Identifiers**

1. CAS No: 109-73-9
2. RTECS No.: EO2975000
3. DOT UN: 1125 68
4. DOT label: Flammable Liquid

- **Appearance and odor**

Butylamine is a colorless, volatile, flammable liquid with an ammonialike odor; the liquid tends to yellow on standing. The odor threshold is reported to be 1.8 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 73.1
2. Boiling point (760 mm Hg): 78°C (172°F)
3. Specific gravity (water = 1): 0.74 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of butylamine): 2.5
5. Melting point: −50°C (−58°F)
6. Vapor pressure at 20°C (68°F): 82 mm Hg
7. Solubility: Miscible with water, alcohol, and ether
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosion may result from contact of butylamine with strong oxidizers or strong acids.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving butylamine.
4. Special precautions: In the presence of moisture, butylamine corrodes some metals on contact.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (dangerous fire hazard) to butylamine.

1. Flash point: −12°C (10°F) (closed cup)
2. Autoignition temperature: 312°C (594°F)
3. Flammable limits in air (% by volume): Lower, 1.7; upper, 9.8
4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving butylamine. Water may be an ineffective extinguishant, but it may be used to cool

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fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving butylamine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of butylamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving butylamine. Firefighters' protective clothing may not provide protection against permeation by butylamine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for butylamine is 5 ppm (15 mg/m^3) as a ceiling limit. A worker's exposure to butylamine shall at no time exceed this ceiling limit. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (15 mg/m^3) as a ceiling limit with a "Skin" notation [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned butylamine a ceiling limit of 5 ppm (15 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH also assigns a "Skin" notation to butylamine [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye, skin, and respiratory tract irritation associated with exposure to butylamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to butylamine can occur through inhalation, ingestion, eye or skin contact, and by skin absorption.

- **Summary of toxicology**

1. *Effects on Animals*: Butylamine vapor is an irritant of the eyes, nose, respiratory tract, and skin; contact of liquid butylamine with the eyes or skin causes corrosive burns. The oral LD_{50} in rats is 366 mg/kg, the LC_{50} in rats is 4,000 ppm for 4 hr, and the dermal LD_{50} in rabbits is 850 mg/kg [NIOSH 1991]. Rats exposed for an unspecified time to butylamine at concentrations of 3,000 to 5,000 ppm exhibited signs of severe irritation of the respiratory tract, developed pulmonary edema, and died within minutes or hours of the exposure [Clayton and Clayton 1981]. When applied to the skin of guinea pigs, butylamine caused necrosis [ACGIH 1991a]. Butylamine caused severe damage to the eyes of rabbits [ACGIH 1991a].

2. *Effects on Humans*: Exposure to butylamine vapor causes eye, nose, and upper respiratory tract irritation, and contact of the skin or eyes with liquid butylamine causes severe irritation, corrosive burns, and possibly blindness [Clayton and Clayton 1981]. Workers exposed to butylamine concentrations at 5 to 10 ppm or higher experience eye and upper respiratory tract irritation, and exposure to butylamine concentrations at 10 to 25 ppm for more than a few minutes is considered intolerable by some workers [Clayton and Clayton 1981; Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: The signs and symptoms of acute exposure to butylamine include redness and tearing of the eyes, runny nose, scratchy throat, headache, facial flushing, increased pulse and respiratory rates, shortness of breath, and (if the exposure is severe) hyperactive reflexes, cyanosis, pulmonary edema, convulsions, and coma. If absorbed through the skin in toxic amounts, butylamine can cause nausea, vomiting, and shock. Direct eye or skin contact with the liquid can result in deep second-degree burns, blistering, corrosion, and possible blindness. Oral administration of near-lethal doses of butylamine to rats and rabbits resulted in hyperactivity of the reflexes, an increase in pulse and respiratory rates, shortness of breath, convulsions, cyanosis, and coma [ACGIH 1991a]. Some workers exposed to this substance at 5 to 10 ppm also experienced headache and facial flushing [Proctor et al. 1988].

2. *Chronic exposure*: No signs or symptoms of chronic exposure to butylamine have been reported.

- **Emergency procedures**

WARNING!

Exposed victims may die!

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of butylamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of butylamine are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if butylamine or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve butylamine and may result in worker exposures to this substance:

—Use of butylamine as a vulcanizing accelerator and reaction initiator in the rubber and polymer industries

—Use of butylamine as a chemical intermediate in the production of emulsifying agents, rubber chemicals, synthetic tanning agents, and special soaps

—Manufacture of photographic developers, pharmaceuticals, dyes, gasoline antioxidants, insecticides, and textile desizing agents

—Use of butylamine as a flavoring ingredient in alcoholic beverages, ice cream, ices, candy, baked goods, gelatins, and puddings

The following methods are effective in controlling worker exposures to butylamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to butylamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to butylamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to butylamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of butylamine on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. However, no biological monitoring test acceptable for routine use has yet been developed for butylamine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne butylamine is determined by using sulfuric-acid-coated silica gel tubes (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 15 liters is collected. The samples are desorbed with methanol/water (50:50). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is not known. This method is described in Method No. S138 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Butylamine causes severe burns on contact with the skin; this substance can also be absorbed through the skin in toxic amounts. Therefore, if butylamine contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min and then wash with soap and water. Get medical attention immediately.

Clothing and shoes contaminated with butylamine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of butylamine, particularly its potential to be absorbed through the skin and to cause eye and skin burns.

A worker who handles butylamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where butylamine or a solution containing butylamine is handled, processed, or stored.

STORAGE

Butylamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard storage area or room for flammable liquids. All ventilation systems and electrical equipment in storage areas should be of explosionproof design. Containers of butylamine should be protected from physical damage and should be stored separately from strong oxidizers and strong acids, heat, sparks, and open flame. To prevent static sparks, all containers and equipment used in shipping, transferring, or receiving operations should be bonded and grounded. Because containers that formerly contained butylamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving butylamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to cool fire-exposed containers and to reduce vapors; such spraying may not prevent ignition in closed spaces.
6. Absorb small spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large spills, build dikes far ahead of the spill to contain the butylamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Butylamine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for butylamine is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of butylamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although butylamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of butylamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with butylamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been recommended for use against permeation by butylamine and may withstand permeation for more than 4 but fewer than 8 hr. Butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl alcohol, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by butylamine.

If butylamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which butylamine might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with butylamine. Contact lenses should not be worn if the potential exists for butylamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL CHROMATE

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl chromate (measured as chromate) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8H_{18}CrO_4$

- **Structure**

$[(CH_3)_3CO]_2CrO_2$

- **Synonyms**

t-Butyl chromate; bis(tert-butyl)chromate; chromic acid, di-tert-butyl ester.

- **Identifiers**

1. CAS No.: 1189-85-1
2. RTECS No.: GB2900000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

tert-Butyl chromate is a clear, colorless liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 230.3
2. Boiling point: Data not available
3. Specific gravity: Data not available
4. Vapor density (air = 1 at boiling point of tert-butyl chromate): 7.9
5. Melting point: -5° to 0°C (23° to 32°F)
6. Vapor pressure: Data not available
7. Solubility: tert-Butyl chromate is miscible with water
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame may ignite the flammable liquid solution used as a carrier for shipping tert-butyl chromate.

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2. Incompatibilities: Contact of tert-butyl chromate with reducing agents and moisture should be avoided, and contact with acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur) may cause a violent reaction.

3. Hazardous decomposition products: Acrid and irritating fumes and poisonous gases may be released in a fire involving tert-butyl chromate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to tert-butyl chromate. Other sources rate tert-butyl chromate as a dangerous fire hazard.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, sand, water spray, or foam to extinguish fires involving tert-butyl chromate.

Fires involving tert-butyl chromate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of tert-butyl chromate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if a rising sound from a venting safety device is heard or if there is discoloration of a container due to fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving tert-butyl chromate. Structural fire-fighters' protective clothing will provide limited protection against fires involving tert-butyl chromate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl chromate (measured as chromate) is 0.1 mg/m^3 as a ceiling limit. A worker's exposure to tert-butyl chromate shall at no time exceed this ceiling level. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers tert-butyl chromate a potential human carcinogen and has issued a recommended exposure limit (REL) for tert-butyl chromate (measured as hexavalent chromium) of 1 g/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl chromate (measured as chromate) a ceiling limit value of 0.1 mg/m^3, which should not be exceeded during any part of the working exposure. The ACGIH also assigns a "Skin" notation to tert-butyl chromate [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the inferred risk of cancer associated with exposure to this substance [NIOSH 1992]. The ACGIH limit is based on the risk of pulmonary changes, narcosis, and necrotic lesions of the skin associated with exposure to this substance [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to tert-butyl chromate can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* tert-Butyl chromate is a hexavalent chromium compound. Although there are no acute toxicity data specifically for this chromate, hexavalent chromium compounds are known to cause cancer in experimental animals, including lung cancers, injection-site tumors, and cancer of the kidneys [Langard 1988]. In contact with the skin of animals, tert-butyl chromate causes necrosis of the skin at the site of contact; death caused by percutaneous absorption of lethal quantities of this substance also occurs [ACGIH 1991]. Rats exposed repeatedly for 30 to 60 minutes/day to an unspecified but lethal concentration of tert-butyl chromate and butyl alcohol showed signs of respiratory and skin irritation and behavioral changes before death [ACGIH 1991]. At autopsy, lung edema and fatty deposition in the liver were seen in these animals [ACGIH 1991]. In another study, exposure of rats to tert-butyl chromate alone (concentration not specified) caused an increase in respiratory rate and signs of mild narcosis [ACGIH 1991].

2. *Effects on Humans:* NIOSH classifies all hexavalent chromium compounds, including tert-butyl chromate, as potential occupational carcinogens. However, there is little toxicity information specifically for organic hexavalent compounds, including tert-butyl chromate. In humans, tert-butyl chromate causes acid-like burns and necrotic lesions in contact with the eyes or skin, and exposure to the vapor of this substance causes irritation of the upper respiratory tract and may lead to ulceration of the nasal septum [NJDH 1987]. Skin contact can also cause an allergic rash in sensitive individuals, and long-term exposure may lead to kidney or liver damage [NJDH 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to tert-butyl chromate include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, nose bleeds, nasal discharge, crusting or sores in the nose, and skin and eye burns.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to tert-butyl chromate include perforation of the nasal septum, jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl chromate! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if tert-butyl chromate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve tert-butyl chromate and lead to worker exposures to this substance:

—Use in specialty reactions as an organic source of chromium

—Manufacture of catalysts

—Use for polymerizing olefins and as a curing agent for urethane resins

The following methods are effective in controlling worker exposures to tert-butyl chromate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to tert-butyl chromate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory tract, kidneys, and liver. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl chromate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin or respiratory allergies or findings consistent with diseases of the eyes, skin, respiratory tract, kidneys, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl chromate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl chromate on the eyes, skin, respiratory tract, kidney, or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary chromium concentrations correlate well with airborne chromium concentrations and are believed to be good indicators of recent short-term exposure. A urinary chromium level of 40-50 g/liter urine, or 30 g per gram creatinine, is believed to correspond to exposure to an airborne chromium level of 0.05 mg/m3 [Baselt 1988].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to tert-butyl chromate may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne tert-butyl chromate is made using a low ash polyvinyl chloride (LAPVC) 5-micron filter. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. The sample is then treated with a carbonate/bicarbonate buffer to extract the tert-butyl chromate. Analysis is conducted by polarographic analysis using differential pulse polarography. This method has a sampling and analytical error of 0.18 and is described in the OSHA Computerized Information System [OSHA 1993] and in Method ID-103 of the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Because tert-butyl chromate can be absorbed through the skin in toxic amounts, workers should immediately wash any affected areas with soap and water.

Clothing contaminated with tert-butyl chromate should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of tert-butyl chromate, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles tert-butyl chromate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where tert-butyl chromate or a solution containing tert-butyl chromate is handled, processed, or stored.

STORAGE

tert-Butyl chromate should be stored in an explosion-proof refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of tert-butyl chromate should be protected from physical damage and should be stored separately from reducing agents, moisture, acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur), heat, sparks, and open flame. Because containers that formerly contained tert-butyl chromate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving tert-butyl chromate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Remove all sources of heat and ignition.
3. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
4. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
5. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl chromate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

tert-Butyl chromate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of tert-butyl chromate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 lb or more or otherwise use 10,000 lb or more of a chromium compound per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of such compounds emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although tert-butyl chromate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl chromate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with tert-butyl chromate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to tert-butyl chromate permeation; however, butyl rubber and polyvinyl chloride have been tested against a chemically similar material (chromic acid) and will potentially resist permeation for periods greater than 4 but fewer than 8 hours. Since specific test data are not available for tert-butyl chromate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to tert-butyl chromate.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl chromate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl chromate. Contact lenses should not be worn if the potential exists for tert-butyl chromate exposure.

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OSHA [1993]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

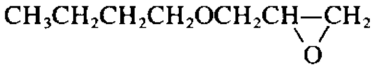
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about n-butyl glycidyl ether (BGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_7H_{14}O_2$
- **Structure:**



$CH_3CH_2CH_2CH_2OCH_2CH{-}CH_2$ (with O bridging CH and CH_2)

- **Synonyms:** BGE; butyl glycidyl ether; 2,3-epoxypropyl butyl ether; 1-butoxy-2,3-epoxypropane
- **Identifiers:** CAS 2426-08-6; RTECS TX4200000; DOT not assigned
- **Appearance and odor:** Colorless to pale yellow liquid with a slightly unpleasant odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.21
2. Boiling point (at 760 mmHg): 164°C (327°F)
3. Specific gravity (water = 1): 0.91
4. Vapor density (air = 1 at boiling point of BGE): 4.5
5. Vapor pressure at 20°C (68°F): 3 mmHg
6. Solubility in water, g/100 g water at 20°C (68°F): 2
7. Evaporation rate (butyl acetate = 1): 0.36
8. Saturation concentration in air (approximate) at 25°C (77°F): 0.42% (4,200 ppm)

- **Reactivity**

1. Incompatibilities: Contact between BGE and strong oxidizing agents may cause fires and explosions. Contact between BGE and strong caustics may cause polymerization with the liberation of heat, which may cause the container to burst. BGE should not be exposed to light or air because explosive peroxides may be formed.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving BGE.
3. Caution: BGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 54°C (130°F) (closed cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class II Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, BGE should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for BGE is 50 parts of BGE per million parts of air (ppm) [270 milligrams of BGE per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 5.6 ppm (30 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 25 ppm (135 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for n-butyl glycidyl ether

	Exposure limits	
	ppm	**mg/m^3**
OSHA PEL TWA	50	270
NIOSH REL Ceiling (15 min)	5.6	30
ACGIH TLV® TWA	25	135

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HEALTH HAZARD INFORMATION

- **Routes of exposure**

BGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: In rats and mice, acute inhalation or oral administration of BGE caused central nervous system depression, pulmonary edema, and death; intramuscular injection in rats produced increased white blood cell counts. Subchronic inhalation of BGE by rats produced testicular atrophy; dermal exposure of male mice that were subsequently bred to unexposed females produced an increased incidence of fetal deaths. BGE was mutagenic in bacterial test systems, and DNA damage was induced *in vitro* in human white blood cells.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to BGE can cause mild irritation of the skin, eyes, nose, and respiratory tract.
2. *Long-term (chronic):* Exposure to BGE can cause inflammation and sensitization of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to BGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and reproductive, nervous, respiratory, and hematopoietic (blood-cell-forming) systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to BGE at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to BGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and reproductive, nervous, respiratory, and hematopoietic systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of BGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting BGE vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure BGE may also be used if available. A detailed sampling and analytical method for BGE may be found in *NIOSH Manual of Analytical Methods* (method number S81).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with BGE.

Workers should be provided with and required to use splash-proof safety goggles where BGE may come in contact with the eyes.

SANITATION

Clothing which is contaminated with BGE should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of BGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of BGE's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with BGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle BGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to BGE may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for BGE

Operations	Controls
During use as a reactive diluent of epoxy resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a chemical intermediate for preparation of ethers, surfactants, polymers, and resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a stabilizing agent for organic chemicals	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to BGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If BGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to BGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If BGE gets on the skin, wash it immediately with soap and water. If BGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If BGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing BGE, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from BGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing BGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. BGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing BGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for n-butyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 56 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection) Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage may require eye protection)
Less than or equal to 140 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection) Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 280 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 3,500 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 3,500 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 5.6 ppm (30 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL LACTATE

INTRODUCTION

This guideline summarizes pertinent information about n-butyl lactate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{14}O_3$

- **Structure**

$CH_3CH(OH)COOC_4H_9$

- **Synonyms**

Butyl α-hydroxypropionate; butyl lactate; 2-hydroxypropanoic acid, butyl ester; lactic acid, butyl ester

- **Identifiers**

1. CAS No.: 138-22-7
2. RTECS No.: OD4025000
3. DOT UN: 1993 27 (combustible liquid not otherwise specified)
4. DOT label: None

- **Appearance and odor**

n-Butyl lactate is a clear, colorless to white, combustible liquid. It has a mild, transient odor. The odor threshold is reported to be 7 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 146.2
2. Boiling point (760 mm Hg): 188°C (370.4°F)
3. Specific gravity (water = 1): 0.9 to 0.984 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butyl lactate): 5.0
5. Melting point: −43°C (−45.4°F)
6. Vapor pressure at 20°C (68°F): 0.4 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol and ether; hydrolyzed by acids and bases
8. Evaporation rate (butyl acetate = 1): 0.44

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. Strong acids (such as hydrochloric, sulfuric, or nitric) and strong bases (such as sodium hydroxide) can cause butyl lactate to decompose.
2. Incompatibilities: A reaction may result from contact of n-butyl lactate with strong oxidizers.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide) may be released in a fire involving n-butyl lactate.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to n-butyl lactate.

1. Flash point: 71°C (160°F) (open cup)
2. Autoignition temperature: 382°C (720°F)
3. Flammable limits in air (% by volume): Lower, 1.15; upper, data not available
4. Extinguishant: Use water fog, dry chemical, alcohol foam, or carbon dioxide to fight fires involving n-butyl lactate. Do not use a solid stream of water because this will scatter and spread the fire. Water may be ineffective for fighting fires, but it may be used to cool fire-exposed containers.

Fires involving n-butyl lactate should be fought upwind and from the maximum distance possible. Isolate the hazard area

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Division of Standards Development and Technology Transfer

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and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-butyl lactate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butyl lactate. Firefighters' protective clothing may not provide protection against permeation by n-butyl lactate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl lactate is 5 ppm (25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (25 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butyl lactate a threshold limit value (TLV) of 5 ppm (30 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of headaches and irritation of pharyngeal and laryngeal mucosa associated with exposure to n-butyl lactate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to n-butyl lactate can occur through inhalation, ingestion, or eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: n-Butyl lactate is an eye and respiratory tract irritant and a central nervous system depressant; it also causes a moderate degree of irritation to the skin of rabbits [NIOSH 1991]. The oral LD_{50} in rats is 5 g/kg [NIOSH 1991]. Acutely poisoned animals exhibit somnolence, flaccid paralysis, and dyspnea before death.

2. *Effects on Humans*: n-Butyl lactate is a central nervous system depressant and an irritant of the eyes, mucous membranes, and upper respiratory tract. Prolonged or repeated contact with the skin by n-butyl lactate causes defatting, redness, and cracking of the skin [Genium 1987]. Prolonged exposures to approximately 7 ppm with peak exposures to 11 ppm caused irritation of the pharyngeal and laryngeal mucosa, coughing, and complaints of sleepiness and headache in the evening after work [ACGIH 1991a]. Some workers also experienced nausea and vomiting [ACGIH 1991a]. Exposure to 4 ppm also caused some of these symptoms [ACGIH 1991a]. No symptoms were reported by workers exposed to n-butyl lactate at concentrations below 1.4 ppm [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-butyl lactate may cause coughing, scratchy throat, nausea, headache, dyspnea, vomiting, CNS depression, and redness, pain, and tearing of the eyes.

2. *Chronic exposure*: Prolonged or repeated contact with n-butyl lactate may cause ocular or mucosal irritation, dryness, redness, cracking, and defatting of the skin.

- **Emergency procedures**

[redacted]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-butyl lactate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-butyl lactate are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-butyl lactate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of n-butyl lactate may result in worker exposures to this substance:

—Use as a solvent for cellulose, varnishes, lacquers, stencil pastes, natural gums, oils, dyes, and many synthetic polymers

—Use in making paint, inks, perfumes, and dry cleaning fluids

—Use in making antiskinning agents and adhesives and as a chemical intermediate

The following methods are effective in controlling worker exposures to n-butyl lactate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to n-butyl lactate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-butyl lactate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-butyl lactate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-butyl lactate on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butyl lactate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butyl lactate is determined by using a charcoal tube (100/50-mg front and backup sections). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with a 95:5 mixture of methylene chloride and methanol to extract the n-butyl lactate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the OSHA Laboratory In-House Methods File [OSHA 1990].

PERSONAL HYGIENE

If n-butyl lactate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with n-butyl lactate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles n-butyl lactate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-butyl lactate or a solution containing n-butyl lactate is handled, processed, or stored.

STORAGE

n-Butyl lactate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet the requirements for OSHA Class IIIA [29 CFR 1910.106] combustible liquids. Containers of n-butyl lactate should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Only nonsparking tools may be used to handle n-butyl lactate. To prevent static sparks, containers and equipment must be grounded and bonded when transferring this material. Because containers that formerly contained n-butyl lactate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-butyl lactate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres using ventilation of explosionproof design.

5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the n-butyl lactate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butyl lactate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of n-butyl lactate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butyl lactate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-butyl lactate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butyl lactate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged skin contact with n-butyl lactate. Impervious gloves, aprons, boots, gauntlets, plastic coveralls, and other protective clothing should be worn as necessary when handling this material. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to n-butyl lactate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to n-butyl lactate.

If n-butyl lactate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-butyl lactate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butyl lactate. Contact lenses should not be worn if the potential exists for n-butyl lactate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about n-butyl mercaptan for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_4H_{10}S$
- **Structure:** $CH_3\text{-}(CH_2)_2\text{-}CH_2\text{-}SH$
- **Synonyms:** n-Butanethiol; 1-butanethiol; butyl sulfhydrate; thiobutyl alcohol
- **Identifiers:** CAS 109-79-5; RTECS EK6300000; DOT 2347, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless liquid with a strong, obnoxious odor like garlic or skunk

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical Data**

1. Molecular weight: 90.19
2. Boiling point (at 760 mmHg): 97.8°C (208°F)
3. Specific gravity (water = 1): 0.8368
4. Vapor density (air = 1 at boiling point of n-butyl mercaptan): 3.1
5. Melting point: -116°C (-177°F)
6. Vapor pressure at 20°C (68°F): 35 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.06
8. Evaporation rate (butyl acetate = 1): 2.86
9. Saturation concentration in air (approximate) at 20°C (68°F): 4.6% (46,000 ppm)
10. Ionization potential: 9.14 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents; n-butyl mercaptan should not be stored in copper or copper-containing materials.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving n-butyl mercaptan.
3. Caution: n-Butyl mercaptan will attack some forms of plastics, coating, and rubber.

- **Flammability**

1. Flash point: 2°C (35°F)
2. Extinguishant: Carbon dioxide, dry chemicals, or foam
3. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 1.0 to 48 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, n-butyl mercaptan can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl mercaptan is 10 parts of n-butyl mercaptan per million parts of air (ppm) [35 milligrams of n-butyl mercaptan per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 0.5 ppm (1.8 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1.5 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for n-butyl mercaptan

	Exposure limit	
	ppm	mg/m^3
OSHA PEL TWA	10	35
NIOSH REL ceiling (15 min)	0.5	1.8
ACGIH TLV® TWA	0.5	1.5

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Butyl mercaptan may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• Summary of toxicology
1. *Effects on animals:* In mice and rats, inhalation of n-butyl mercaptan caused increased breathing rates, hyperactivity, uncoordinated movement, staggering gait, muscular weakness, partial skeletal muscle paralysis, deficient oxygenation of the blood (cyanosis), sedation, and death.
2. *Effects on humans:* In an industrial accident, seven workers were exposed to n-butyl mercaptan for approximately 1 hour at a concentration estimated between 50 and 500 ppm; all workers experienced some of the symptoms listed below, although the specific combination of symptoms varied for each individual.

• Signs and symptoms of exposure
Short-term (acute): Exposure to n-butyl mercaptan can cause irritation of the mucous membranes, weakness, malaise, increased respiration, neck pain, drowsiness, nausea, vomiting, sweating, dizziness, confusion, and coma.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to n-butyl mercaptan, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risk. These should concentrate on the function and integrity of the nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to n-butyl mercaptan at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the respiratory system.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to n-butyl mercaptan. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of n-butyl mercaptan. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting n-butyl mercaptan vapors with Chromosorb 104 tubes, followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure n-butyl mercaptan may be used if available. A detailed sampling and analytical method for n-butyl mercaptan may be found in the *NIOSH Manual of Analytical Methods* (method number S350).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with n-butyl mercaptan.

Workers should be provided with and required to use splash-proof safety goggles where n-butyl mercaptan may come in contact with the eyes.

SANITATION

Clothing which is contaminated with n-butyl mercaptan should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of n-butyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of n-butyl mercaptan's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with n-butyl mercaptan should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle n-butyl mercaptan should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to n-butyl mercaptan may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for n-butyl mercaptan

Operations	Controls
During the manufacture and processing of n-butyl mercaptan; during use as an odorant for natural gas	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a chemical intermediate in the manufacture of agricultural chemicals, herbicides, and defoliants	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the polymer industry in the manufacture of polymerization catalysts, stabilizers, modifiers, and chain transfer agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a solvent; during the cleaning and maintenance of storage vessels and equipment	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to n-butyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If n-butyl mercaptan gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to n-butyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If n-butyl mercaptan gets on the skin, wash it immediately with soap and water. If n-butyl mercaptan penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the location of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If n-butyl mercaptan is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing n-butyl mercaptan, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from n-butyl mercaptan vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing n-butyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. n-Butyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing n-butyl mercaptan may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for n-butyl mercaptan

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator
	Any self-contained breathing apparatus
	Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 12.5 ppm	Any supplied-air respirator operated in a continuous flow mode
	Any powered air-purifying respirator with organic vapor cartridge(s)
Less than or equal to 25 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s)
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
Less than or equal to 500 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 1,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any suppplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 ppm (1.8 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-sec-BUTYLPHENOL

INTRODUCTION

This guideline summarizes pertinent information about o-sec-butylphenol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{14}O$

- **Structure**

$C_2H_5(CH_3)CHC_6H_4OH$

- **Synonyms**

2-(1-Methylpropyl)phenol; 2-sec-butylphenol

- **Identifiers**

1 CAS No.: 89-72-5

2. RTECS No.: SJ8920000

3. DOT UN: 2228 53

4. DOT label: St. Andrew's Cross

- **Appearance and odor**

o-sec-Butylphenol is a colorless, slightly volatile, combustible liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 150.2

2. Boiling point (760 mm Hg): 226° to 228°C (438.8° to 442°F)

3. Specific gravity (water = 1): 0.98 at 20°C (68°F)

4. Vapor density: Data not available

5. Melting point: 16°C (60.9°F)

6. Vapor pressure at 20°C (68°F): Data not available; however, o-sec-butylphenol is reported to be slightly volatile.

7. Solubility: Insoluble in water; soluble in alcohol, ether, and alkalies

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: None known

3. Hazardous decomposition products: Toxic gases may be released in a fire involving o-sec-butylphenol.

4. Special precautions: None known

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to o-sec-butylphenol; other sources report that this substance is combustible but does not ignite readily.

1. Flash point: 107.2°C (225°F)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol to fight fires involving o-sec-butylphenol.

Fires involving o-sec-butylphenol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of o-sec-butylphenol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not

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possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving o-sec-butylphenol. Chemical protective clothing that is specifically recommended for o-sec-butylphenol may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by o-sec-butylphenol.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for o-sec-butylphenol is 5 ppm (30 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (30 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-sec-butylphenol a threshold limit value (TLV) of 5 ppm (31 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to o-sec-butylphenol [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye and respiratory irritation and skin burns associated with exposure to o-sec-butylphenol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-sec-butylphenol can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: o-sec-Butylphenol is an irritant of the eyes, skin, and upper respiratory tract. Application of 0.05 mg of o-sec-butylphenol to the eyes of rabbits caused severe injury [NIOSH 1991; ACGIH 1991a]. When applied to the skin of rabbits for 24 hr, 500 mg caused severe burns [ACGIH 1991a; NIOSH 1991]. The dermal LD_{50} in guinea pigs is 600 mg/kg [NIOSH 1991]. Rats survived a 7-hr exposure to an atmosphere saturated with o-sec-butylphenol vapor [ACGIH 1991a]. The oral LD_{50} is 2,700 mg/kg in rats and 600 mg/kg in guinea pigs [NIOSH 1991]. This material was nonmutagenic when tested in five strains of *Salmonella typhimurium* [NLM 1991].

2. *Effects on Humans*: o-sec-Butylphenol is an eye, skin, and respiratory tract irritant and a potential corrosive. Acute occupational exposures to unspecified concentrations of this substance cause mild respiratory tract irritation, and prolonged skin contact results in dermal ulcerations and burns [ACGIH 1991a; NLM 1991]. Ingestion of a solution exceeding 5% o-sec-butylphenol may cause oral burns, which can become necrotic several days later [NLM 1991]. Using analogous data from other phenolic compounds, it may also cause nausea, vomiting, intense sweating, diarrhea, methomoglobinemia, tachycardia, hypotension, arrhythmias, seizures, CNS depression, hepatic injury, and death from respiratory arrest [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to o-sec-butylphenol can cause eye irritation, redness, and pain; irritation of the nasal and respiratory tract mucosa; scratchy throat; and redness, swelling, and chemical burns of the skin.

2. *Chronic exposure*: Other than irritation, no signs or symptoms of chronic exposure to o-sec-butylphenol have been reported.

- **Emergency procedures**

[illegible]

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of o-sec-butylphenol! ***Immediately but gently***

flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of o-sec-butylphenol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if o-sec-butylphenol or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The preparation of plasticizers, resins, surface-active agents, and other products may involve o-sec-butylphenol and may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to o-sec-butylphenol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to o-sec-butylphenol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-sec-butylphenol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-sec-butylphenol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-sec-butylphenol on the respiratory tract and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-sec-butylphenol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-sec-butylphenol is determined by using a XAD-7 tube (100/50-mg sections; 15/50 mesh). Samples are collected at a recommended flow rate of 0.1 liter/min until a recommended air volume of 10 liters is collected. Analysis is conducted by high-performance liquid chromatography using ultraviolet light. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the OSHA Laboratory In-House Methods File [OSHA 1990].

PERSONAL HYGIENE

Because o-sec-butylphenol can be absorbed through the skin in toxic amounts, workers should immediately and thoroughly wash with soap and water any areas of the skin that have contacted this substance.

Clothing and shoes contaminated with o-sec-butylphenol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of o-sec-butylphenol, particularly its potential for being an irritant and for being absorbed through the skin in toxic amounts.

A worker who handles o-sec-butylphenol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where o-sec-butylphenol or a solution containing it is handled, processed, or stored.

STORAGE

o-sec-Butylphenol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-sec-butylphenol should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained o-sec-butylphenol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-sec-butylphenol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Absorb liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

o-sec-Butylphenol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-sec-butylphenol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-sec-butylphenol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-sec-butylphenol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-sec-butylphenol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with o-sec-butylphenol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-sec-butylphenol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-sec-butylphenol.

If o-sec-butylphenol is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-sec-butylphenol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-sec-butylphenol. Contact lenses should not be worn if the potential exists for o-sec-butylphenol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR p-tert-BUTYLTOLUENE

INTRODUCTION

This guideline summarizes pertinent information about p-tert-butyltoluene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{11}H_{16}$

- ***Synonyms***

1-Methyl-4-tert-butylbenzene; 1-tert-butyl-4-methylbenzene; 4-tert-butyltoluene; 1-(1,1-dimethyl)-4-methylbenzene; p-methyl-tert-butylbenzene; TBT; p-TBT

- **Identifiers**

1. CAS No.: 98-51-1
2. RTECS No.: XS8400000
3. DOT UN (for butyltoluenes): 2667 27
4. DOT label (for butyltoluenes): St. Andrew's Cross

- **Appearance and odor**

p-tert-Butyltoluene is a clear, colorless, combustible liquid with a gasoline-like odor. The odor threshold is reported to be 5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 148.3
2. Boiling point (at 760 mm Hg): 192.8°C (379°F)
3. Specific gravity (water = 1): 0.86 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of p-tert-butyltoluene): 4.6
5. Melting point: −55°C (−67°F)
6. Vapor pressure at 25°C (77°F): 0.65 mm Hg
7. Solubility: Insoluble in water; slightly soluble in alcohol; very soluble in ether; miscible with most common industrial solvents
8. Evaporation rate (butyl acetate = 1): Very low

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of p-tert-butyltoluene with oxidizing materials.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released when p-tert-butyltoluene decomposes.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to p-tert-butyltoluene. Other sources rate p-tert-butyltoluene's fire hazard as moderate.

1. Flash point: 68°C (155°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use carbon dioxide, dry chemical, foam, or water fog to fight fires involving p-tert-butyltoluene. Do not use a solid stream of water because the stream will scatter and spread the fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for p-tert-butyltoluene is 10 ppm (60 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 20 ppm (120 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (60 mg/m^3) as an 8-hr TWA and 20 ppm (120 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned p-tert-butyltoluene a threshold limit value (TLV) of 10 ppm (61 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek, and a STEL of 20 ppm (121 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation, nausea, and central nervous system and cardiovascular effects associated with exposure to p-tert-butyltoluene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to p-tert-butyltoluene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: p-tert-Butyltoluene is a mild eye, skin, and respiratory tract irritant and a central nervous system depressant in animals acutely exposed; chronic exposure causes lung, brain, liver, and kidney damage. p-tert-Butyltoluene caused slight and transient eye irritation in rats and mild skin irritation in rabbits [NIOSH 1991; Grant 1986]. The dermal LD_{50} in rabbits is 19,600 mg/kg, and the LC_{50} in rats is 934 ppm for 1 hr [NIOSH 1991]. The oral LD_{50} in rats is 1,800 mg/kg. Acutely poisoned animals showed signs of eye and respiratory tract irritation and central nervous system effects including convulsions before death [Hine et al. 1954]. Rats repeatedly inhaling 25 or 50 ppm for 1 to 7 hr showed an increase in hemoglobin and a decrease in both erythrocyte and leukocyte counts [Clayton and Clayton 1981]. Repeated exposure of rats to 50 ppm caused liver and kidney changes and lesions of the brain and spinal cord [Hine et al. 1954]. Rats repeatedly exposed to 850 ppm for 1 hr progressively showed tremor, clonic movements, and flexor paralysis; pulmonary edema and pneumonia were the most frequent causes of death in animals after 10 such exposures [NLM 1990].

2. *Effects on Humans*: p-tert-Butyltoluene causes eye, skin, and upper respiratory tract irritation and central nervous system effects in humans. The irritant dose for the human eye is 5 ppm for 2 hr [NIOSH 1991]. The lowest acute toxic concentration in humans is 20 ppm for 5 min; central nervous system effects are seen at this concentration. Volunteers exposed for 5 min to p-tert-butyltoluene at concentrations ranging from 5 to 160 ppm reported experiencing nausea, upper respiratory tract irritation, and a metallic taste in the mouth. Volunteers exposed to the 160-ppm concentration became giddy and had increased pulse rates [Hine et al. 1954]. Workers chronically exposed to concentrations that were generally below 10 ppm reported anxiety and experienced decreased blood pressure, increased pulse rate, tremor, hematologic changes, and skin irritation [Hine et al. 1954].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to p-tert-butyltoluene can cause contact irritation, runny nose, scratchy throat, headache, tiredness, giddiness, anxiety, nausea, metallic taste, weakness, tremor, ataxia, increased pulse rate, decreased blood pressure, dizziness, confusion, hallucinations, dysarthria, convulsions, dyspnea, increased breathing effort, temporary loss of consciousness, and death from possible respiratory failure [NLM 1990].

2. *Chronic exposure*: Repeated or prolonged contact of p-tert-butyltoluene causes defatting and irritation of the skin. It can also cause tremor, decreased blood pressure, elevated pulse rate, and blood changes.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of p-tert-butyltoluene. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of p-tert-butyltoluene are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose to remove residues from nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if p-tert-butyltoluene or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve p-tert-butyltoluene and may result in worker exposures to this substance:

—Production of resins

—Use of p-tert-butyltoluene as a primary intermediate and as a solvent in the chemical and pharmaceutical industries

The following methods are effective in controlling worker exposures to p-tert-butyltoluene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to p-tert-butyltoluene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory system, blood, and central nervous system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to p-tert-butyltoluene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, respiratory system, blood, or central nervous system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to p-tert-butyltoluene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of p-tert-butyltoluene on the eyes, skin, respiratory system, blood, and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for p-tert-butyltoluene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of *job transfer or termination. Any changes in the worker's* health status should be compared with those expected for a suitable reference population. Because occupational exposure to p-tert-butyltoluene may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne p-tert-butyltoluene is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 29 liters is collected. The samples are desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.001 to 0.01 mg per sample. This method is described in Method No. 1501 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If p-tert-butyltoluene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, followed by washing with soap and water.

Clothing and shoes contaminated with p-tert-butyltoluene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of p-tert-butyltoluene, particularly its potential for causing irritation of the eyes and skin.

A worker who handles p-tert-butyltoluene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where p-tert-butyltoluene or a solution containing p-tert-butyltoluene is handled, processed, or stored.

STORAGE

p-tert-Butyltoluene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 *CFR 1910.1200*]. The storage area must meet OSHA requirements for a Class IIIA flammable liquid [29 CFR 1910.106]. Ventilation fans and other electrical service must be of explosionproof design. Containers of p-tert-butyltoluene should be protected from physical damage and should be stored separately from oxidizers, heat, sparks, and open flame. Containers of p-tert-butyltoluene should be routinely inspected for leaks. To prevent static sparks, metal containers and equipment must be grounded and bonded during transfers. Because containers that formerly contained p-tert-butyltoluene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving p-tert-butyltoluene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.

5. Use water spray to reduce vapors, but be aware that the spray may not prevent ignition in closed spaces.

6. Use only nonsparking tools for cleanup.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the p-tert-butyltoluene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

p-tert-Butyltoluene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of p-tert-butyltoluene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of p-tert-butyltoluene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although p-tert-butyltoluene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of p-tert-butyltoluene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with p-tert-butyltoluene. Gloves, aprons, boots, and other protective clothing and equipment should be used as necessary to prevent skin contact. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by p-tert-butyltoluene and have demonstrated good-to-excellent resistance for periods greater than 8 hr: polyvinyl alcohol and Viton®. Nitrile rubber may withstand permeation for more than 4 but fewer than 8 hr. Butyl rubber, natural rubber, and neoprene have demonstrated poor resistance to permeation by p-tert-butyltoluene.

If p-tert-butyltoluene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which p-tert-butyltoluene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with p-tert-butyltoluene. Contact lenses should not be worn if the potential exists for exposure to p-tert-butyltoluene.

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Occupational Health Guideline for Cadmium Dust (as Cadmium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all cadmium dust. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Cadmium metal dust

- Formula: Cd
- Synonyms: None
- Appearance and odor: Odorless, gray powder.

Cadmium oxide dust

- Formula: CdO
- Synonyms: None
- Appearance and odor: Odorless, brown solid or blue-black solid.

Cadmium sulfide dust

- Formula: CdS
- Synonyms: Greenockite
- Appearance: Yellow-orange solid.

Cadmium chloride dust

- Formula: $CdCl_2$
- Synonyms: None
- Appearance: White solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium dust is 0.2 milligram of cadmium dust per cubic meter of air (mg/m^3) averaged over an eight-hour work shift, with a ceiling level of 0.6 mg/m^3. NIOSH has recommended that the permissible exposure limit be reduced to 40 micrograms of cadmium per cubic meter of air (μg/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 200 μg/m^3 averaged over a 15-minute period. The recommendations in this guideline supplement the recommendations in the NIOSH Criteria Document for Cadmium, which should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cadmium dust can affect the body if it is inhaled. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Cadmium dust may cause irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur. Ingestion of cadmium dust may cause nausea, vomiting, diarrhea, and abdominal cramps.
2. *Long-term Exposure:* Repeated or prolonged exposure to cadmium dust may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium has also been reported to cause an increased incidence of cancer of the prostate in man. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium dust.

- **Recommended medical surveillance**

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

The following medical procedures should be made available to each employee who is exposed to cadmium dust at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, liver, kidneys, prostate, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. In addition, the urine should be examined for low molecular weight proteins by use of 3% sulfosalicylic or other acceptable techniques.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease. Urine protein measurements should be made available every four months.

- **Summary of toxicology**

Cadmium dust causes both acute and chronic effects. It is less toxic than cadmium fume, because dust has a larger particle size than fume; at high concentrations of the dust, physiologic effects similar to those arising from fume exposure could be expected. The acute effects primarily involve the lungs but may also affect other organ systems. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m^3 for 1 hour, or 9 mg/m^3 for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m^3, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristical nasopharyngeal irritation followed by a feeling of chest constriction or substernal pain, with persistent cough and dyspnea; there may also be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop and progress rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. Cyanosis may be intense. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days after exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Absorbed cadmium is retained to a large extent by the body, and excretion is very slow. Continued exposure to low levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of an emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of water, beans, and rice contaminated with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; severe pain in the back and joints, a waddly gait, osteomalacia, spontaneous fractures, and occasional fatal renal failure are characteristics of the disorder, which has been termed "itai-itai." Subcutaneous injection of cadmium metal suspended in fowl serum produced rhabdomyosarcomata in rats; cadmium sulfate in sterile distilled water produced sarcomata; and cadmium chloride solution produced pleomorphic sarcomata at the injection site. Increased incidence of prostatic cancer has been reported following occupational exposure to cadmium. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring; acute necrosis of rat testes follows large doses orally or parenterally, but testicular effects have not been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Cadmium metal dust**

1. Molecular weight: 112.4
2. Boiling point (760 mm Hg): 767 C (1412 F)
3. Specific gravity (water = 1): 8.642
4. Vapor density (air = 1 at boiling point of cadmium metal dust): Not applicable
5. Melting point: 321 C (609 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cadmium oxide dust**

1. Molecular weight: 128.4
2. Boiling point (760 mm Hg): 900 C (1652 F) (sublimes and decomposes)
3. Specific gravity (water = 1): 6.95 or 8.15
4. Vapor density (air = 1 at boiling point of cadmium oxide dust): Not applicable
5. Melting point: 900 C (1652 F) (sublimes and decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0005
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cadmium sulfide dust**

1. Molecular weight: 144.5
2. Boiling point (760 mm Hg): Sublimes in N_2 at 980 C (1796 F)
3. Specific gravity (water = 1): 4.82
4. Vapor density (air = 1 at boiling point of cadmium sulfide dust): Not applicable
5. Melting point: 1750 C (3182 F) at 100 atm.
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0001
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cadmium chloride dust**

1. Molecular weight: 183
2. Boiling point (760 mm Hg): 960 C (1760 F)
3. Specific gravity (water = 1): 4.047
4. Vapor density (air = 1 at boiling point of cadmium chloride dust): Not applicable
5. Melting point: 568 C (1054 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 140
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of cadmium metal dust with strong oxidizers or with elemental sulfur, selenium, and tellurium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as cadmium oxide fume) may be released in a fire involving cadmium dust.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 250 C (482 F) (layer) (cadmium metal dust)
3. Minimum explosive dust concentration: Data not available
4. Extinguishant: Dry powder for metal fires

- **Warning properties**

Grant states that "cadmium is a very toxic metal which gives off fumes when burned or heated strongly. Characteristically these fumes cause dryness and irritation of the throat, followed in a few hours by nausea and diarrhea. Smarting of the eyes occurs relatively infrequently, and no injury to the eyes of human beings has been reported. Neither eye nor respiratory irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cadmium dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of cadmium dust on a filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for cadmium dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- If employees' clothing has had any possibility of being contaminated with cadmium dust, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with cadmium dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cadmium dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cadmium dust, the person performing the operation should be informed of cadmium dust's hazardous properties.
- Employees should be provided with and required to use dust-resistant safety goggles where there is any possibility of cadmium chloride dust contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to cadmium chloride dust, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with cadmium dust should wash with soap or mild detergent and water any areas of the body which may have contacted cadmium dust at the end of each work day.
- Eating and smoking should not be permitted in areas where cadmium dust is handled, processed, or stored.
- Employees who handle cadmium dust should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fabrication of cadmium-plated marine, aircraft, and motor vehicle equipment for corrosion-resistant coatings	Local exhaust ventilation; personal protective equipment
Liberation during processing of cadmium metal	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation in synthesis of cadmium compounds	Process enclosure; local exhaust ventilation
Liberation in manufacture and fabrication of cadmium alloys; recovery from flue dusts during smelting of lead and zinc operations	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of nuclear reactor rods	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cadmium dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If cadmium dust gets on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the close of work.

- **Breathing**

If a person breathes in large amounts of cadmium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When cadmium dust or liquids containing cadmium dust have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If cadmium dust is released in hazardous concentrations, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of release.
3. Collect released material in the most convenient and safe manner for reclamation or for disposal in sealed conainers in a secured sanitary landfill.

- Waste disposal method:

Cadmium dust may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

RESPIRATORY PROTECTION FOR CADMIUM DUST (AS CADMIUM)

Condition	**Minimum Respiratory Protection*** **Required Above 0.2 mg/m³**
Dust Concentration	
1 mg/m³ or less	Any dust respirator, except single-use.
2 mg/m³ or less	Any dust respirator, except single-use or quarter-mask respirator. Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Cadmium Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cd/CdO
- Synonyms: None
- Appearance: Finely divided solid particles dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium fume is 0.1 milligram of cadmium fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift, with an acceptable ceiling level of 0.3 mg/m^3. NIOSH has recommended that the permissible exposure limit be reduced to a time-weighted average of 40 micrograms cadmium per cubic meter (ug/m^3) with a ceiling level of 200 ug cadmium/m^3 for a 15-minute period. The NIOSH Criteria Document for Cadmium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cadmium fume can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Cadmium fume causes irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to cadmium fume may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium fume has also been reported to cause an increased incidence of cancer of the prostate in men. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring. This effect has not been reported in humans.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cadmium fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, kidneys, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be examined for the specific protein.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

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Urine protein measurements should be made available every four months.

- **Summary of toxicology**

Cadmium fume (cadmium oxide) is a severe pulmonary irritant that has caused fatal pulmonary edema in workers; chronic exposures may lead to severe pulmonary emphysema. Cadmium sulfide produces malignant tumors in animals by injection, suggesting that cadmium is carcinogenic. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m³ for 1 hour, or 9 mg/m³ for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m³, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristically nasopharyngeal irritation, followed by a feeling of chest constriction or substernal pain, with cough and dyspnea; there also may be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days of exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Continued exposure to lower levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with evidence of renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. Cadmium absorbed by any route is, to a very large extent, retained by the body. Excretion is very slow. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of beans, rice and water contaminated with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; pain in the back and joints, an unsteady gait, osteomalacia, bone fractures, and occasional renal failure are characteristics of the disorder. Rats, injected subcutaneously with cadmium metal suspended in fowl serum, produced rhabdomyosarcomata; with cadmium sulfate in sterile distilled water, sarcomata; and with cadmium chloride solution, pleomorphic sarcomas at the injection site, suggesting that cadmium is carcinogenic. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring. Increased prostatic and lung cancer has been reported in humans exposed to cadmium oxide. Acute necrosis of the rat testis follows large doses orally or parenterally.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 112 — 128
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): Not applicable
  4. Vapor density (air = 1 at boiling point of cadmium fume): Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Not applicable
- **Flammability**
  1. Not applicable
- **Warning properties**

Grant reports that "smarting of the eyes occurs relatively infrequently (upon exposure to cadmium fume), and no injury to the eyes of human beings has been reported. Neither eye nor respiratory tract irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cadmium fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of cadmium fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for cadmium fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

- Eating and smoking should not be permitted in areas where fumes may be generated in the handling or processing of cadmium.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during smelting and refining of ores where it is a by-product of zinc, lead, and copper-bearing ores	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during recovery of metal by processing of scrap; during melting and pouring of cadmium metal; during casting of alloys for cadmium-copper, cadmium-lead, cadmium-bismuth, cadmium-silver, cadmium-nickel, cadmium-lead-silver, cadmium-lead-silver-nickel, cadmium-lead-bismuth-tin, and cadmium-gold products used for coating telephone cables, trolley wires, welding electrodes, automatic sprinkling systems, steam boilers, fire alarms, high-pressure/temperature bearings, starting switches, aircraft relays, light-duty circuit breakers, low-temperature solder, and jewelry	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during fabrication of metal, alloys, or plated steel	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during casting and use of solders; during melting of cadmium ingots for paint and pigment manufacture used for coloring of plastics and ceramic glazes, electroplating, and in chemical synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during coating on metals by hot dipping or spraying	Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during manufacture of nickel-cadmium batteries for use in radio-portable telephones, convenience appliances, and vented cells used in air planes, heliocopters, and stand-by power and lighting	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of cadmium fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of cadmium fume are inadvertently released, ventilate the area of the release to disperse the fume.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

RESPIRATORY PROTECTION FOR CADMIUM FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 mg/m³ or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

DHHS (NIOSH) Publication No. 88-118, Supplement I-OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer
Cincinnati, Ohio

1988

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

NOTE TO THE READER

These 35 occupational safety and health guidelines are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes data on chemical names and synonyms, chemical and physical properties, exposure limits, signs and symptoms of exposure, as well as recommendations for medical monitoring, respiratory and personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers achieve a sound occupational health program.

The recommendations and information contained in these guidelines may be superseded as new information becomes available; readers are advised to regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

This document supplements the 1981 publication entitled NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). Readers may wish to insert each guideline at the appropriate place in that 3-volume set.

CONTENTS

OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

DHHS (NIOSH) Publication No. 89-104, Supplement II-OHG

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NOTICE

The guidelines in Supplement I are not packaged in the exact order listed in the contents. Please add them to your notebook binders in alphabetical order, as indicated in the table of contents.

CONTENTS

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CARBONATE

INTRODUCTION

This guideline summarizes pertinent information about calcium carbonate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaCO_3$

- **Synonyms**

  Aragonite, agricultural limestone, agstone, Bell mine pulverized limestone, calcite, chalk, domolite, franklin, limestone, lithographic stone, marble, Portland Stone, Sohnhofen stone

- **Identifiers**

1. CAS No.: 1317-65-3
2. RTECS No.: EV9580000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

  Calcium carbonate is a noncombustible, odorless, white powder or colorless crystalline solid. Calcium carbonate occurs naturally in the minerals aragonite, calcite, limestone, marble, and vaterite. The two natural forms of calcium carbonate that are important commercially are aragonite and calcite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100.09
2. Boiling point: Not applicable
3. Specific gravity at 20°C (68°F) (water = 1): 2.83 (aragonite); 2.71 (calcite)
4. Vapor density: Not applicable
5. Melting point: 825°C (1,517°F) (aragonite); 1,339°C (2,442°F) (calcite)
6. Vapor pressure: Not applicable
7. Solubility: Insoluble in water and alcohol; soluble in dilute acids.
8. Evaporation rate: Not applicable

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Education and Information Division

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Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of calcium carbonate with acids, alum, ammonium salts, or mercury and hydrogen causes a reaction, and contact with fluorine causes ignition.
3. Hazardous decomposition products: Toxic particulates (such as calcium oxide) may be released in a fire involving calcium carbonate.
4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium carbonate; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium carbonate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium carbonate.

XPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium carbonate is 15 mg/m^3 of air (total dust) and 5 mg/m3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium carbonate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to calcium carbonate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium carbonate can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium carbonate causes moderate-to-severe irritation in contact with the tissues of animals. Instilled into rabbits' eyes, calcium carbonate caused severe irritation [NIOSH 1991]. In contact with the skin of rabbits for 24 hr, this substance caused moderate irritation [NIOSH 1991]. The oral LD_{50} in rats is 6,450 mg/kg [NIOSH 1991].
2. *Effects on Humans:* Calcium carbonate dust is a physical irritant of the eyes, nose, mucous membranes, and skin of humans. Contact of calcium carbonate dust with the eyes causes redness, pain, and inflammation of the eyelids while contact with the skin causes local irritation of moderate degree [NLM 1991]. Exposure to large amounts of the dust of this substance causes coughing, sneezing, and nasal irritation [NLM 1991]. Although chronic exposure to pure calcium carbonate does not cause pneumoconiosis, similar exposure to impure limestone (calcium carbonate) containing 3% to 20% quartz may pose a silicosis risk [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Overexposure to calcium carbonate

dust can cause irritation of the eyelids; redness, tearing, and pain in the eyes; runny nose; sneezing; and coughing. Contact with the skin causes dryness and irritation.

2. *Chronic exposure:* Although no signs or symptoms of chronic exposure to calcium carbonate have been reported, quartz contamination of limestone in excess of 2% may pose a silicosis risk.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium carbonate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** induce vomiting if calcium carbonate has been mixed with a petroleum distillate such as kerosene or diesel fuel.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve calcium carbonate and may result in worker exposures to this substance:

—Use as a neutralizing agent, filler, and extender in rubber, plastic, and paint products, and as an opacification agent in paper products

—Use in the manufacture of putty, tooth powders, antacids, whitewash, quicklime, Portland cement, dentifrices, ceramics, polishes, insecticides, inks, shoe dressings, foods, cosmetics, pharmaceuticals, antibiotics, adhesives, matches, pencils, crayons, linoleum, welding rods, and insulating compounds

—Use in removing sulfur dioxide from stack gases and as a metallurgical flux

—Use in analytical chemistry to detect and measure halogens in organic combinations and in the laboratory generation of carbon dioxide

—Use as a pigment and as a source of lime

—Use in human and veterinary medicine as an antacid.

—As a dietary supplement, as a nutrient, and as an antidiarrheal agent

The following methods are effective in controlling worker exposures to calcium carbonate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to toxic substances should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium carbonate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium carbonate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium carbonate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium carbonate on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium carbonate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

The OSHA method for determining worker exposures to airborne concentrations of calcium carbonate (total dust) is made using a tared, low-ash polyvinyl chloride filter (LAPCF) with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System as Dust, Total [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1987]. NIOSH has a similar method (Method 0500) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984a] which also involves gravimetric analysis. In the NIOSH method, samples are collected at a flow rate of 1.5 to 2 liters/min. The minimum sample volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum is 133 liters. The overall precision for the NIOSH method is 0.056.

The OSHA method for determining worker exposures to airborne concentrations of calcium carbonate (respirable fraction) is made using a tared, low-ash polyvinyl chloride filter (LAPCF) with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is held in a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 800 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System as Dust (Respirable Nuisance) [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1987]. NIOSH has a similar method (Method 0600) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984b], which also involves gravimetric analysis. In the NIOSH method, samples are collected at a flow rate of 1.7 liter/min. The minimum sample volume for an airborne concentration of 5 mg/m^3 is 75 liters, and the maximum is 1,000 liters. The overall precision for the NIOSH method ranges from 0.043 to 0.145 in laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium carbonate collects on the skin in large quantities, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium carbonate should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium carbonate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium carbonate is handled, processed, or stored.

STORAGE

Calcium carbonate should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of calcium carbonate should be protected from physical damage and should be stored separately from acids, alum, ammonium salts, fluorine, mercury, hydrogen, heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a major spill involving calcium carbonate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a major spill:

1. For small spills, vacuum or wet down the spilled material and place into waste containers for disposal.

2. For large spills, wet down the material and dike for later disposal.

3. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Calcium carbonate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium carbonate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium carbonate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21–261.24. Although calcium carbonate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium carbonate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with calcium carbonate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium carbonate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium carbonate.

If calcium carbonate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium carbonate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium carbonate. Contact lenses should not be worn if the potential exists for calcium carbonate exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CYANAMIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium cyanamide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaCN_2$

- **Structure**

  Ca:NCN

- **Synonyms**

  Aero-cyanamid; cyanamide, calcium salt; aero cyanamid granular; calcium carbimide; aero cyanamid special grade; Alzodef; lime-nitrogen; nitrogen lime; nitrolim, nitrolime

- **Identifiers**

  1. CAS No.: 156-62-7

  2. RTECS No.: GS6000000

  3. DOT UN: 1403 40 (not hydrated, containing more than 0.1% calcium carbide)

  4. DOT label: None (not hydrated, containing more than 0.1% calcium carbide)

- **Appearance and odor**

  Calcium cyanamide is a noncombustible, colorless, gray, or black crystalline solid or powder. No information is available on the odor of this substance. The commercial grade may contain a small amount of calcium carbide, which may produce acetylene in closed containers and vessels.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 80.11

  2. Boiling point (760 mm Hg): Sublimes at 1,150° to 1,200°C (2,102° to 2,192°F)

  3. Specific gravity (water = 1): 2.29 at 20°C (68°F)

  4. Vapor density: Data not available

  5. Melting point: 1,340°C (2,444°F)

  6. Vapor pressure: Not volatile

  7. Solubility: Decomposes in water to liberate acetylene gas and ammonia

  8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: Moisture

2. Incompatibilities: Contact with any form of moisture (ice, steam, moist air, water) causes calcium cyanamide to decompose, liberating acetylene and ammonia. Contact with all solvents tested also causes calcium cyanamide to decompose.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving calcium cyanamide.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium cyanamide. In pure form, this substance is not combustible; however, the commercial product may contain calcium carbide, which may liberate very flammable gases and vapors on contact with moisture.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, soda ash, sand, or lime to fight fires involving calcium cyanamide. Do not use foam or water. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving calcium cyanamide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium cyanamide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium cyanamide. Structural firefighters' protective clothing may not provide protection against permeation by calcium cyanamide.

EXPOSURE LIMITS

- **OSHA PEL**

  The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for calcium cyanamide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

  The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

  The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium cyanamide a threshold limit value (TLV) of 0.5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

  The ACGIH limit is based on the risk of irritation and vasomotor effects associated with exposure to calcium cyanamide [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

  Exposure to calcium cyanamide can occur through inhalation, eye or skin contact, dermal absorption, or ingestion.

- **Summary of toxicology**

  1. *Effects on Animals:* Calcium cyanamide can be a severe irritant of the eyes and skin in animals. In pure water or alkaline solutions, it may polymerize to dicyandiamide, a less toxic product. When instilled into rabbits' eyes, the dust of this material was quite irritating [ACGIH 1991]. When applied as a paste to the clipped skin of rabbits under occlusion for 24 hr, a 10-g/kg dose of calcium cyanamide killed two of five rabbits; all animals survived when the dosage was reduced to 5 g/kg [ACGIH 1991]. All surviving animals developed severe skin irritation several days

after application [ACGIH 1991]. In marked contrast to the previous data concerning rabbit dermal lethality, other investigators reported the dermal LD_{50} in rabbits to be 590 mg/kg [NIOSH 1991]. The lowest lethal concentration in rats is 86 mg/m^3 for 4 hr [ACGIH 1991]. The oral LD_{50} in rats is 158 mg/kg [NIOSH 1991]. Calcium cyanamide is mutagenic in bacterial test systems [NIOSH 1991; NLM 1992]. Rats and mice fed a diet containing 63 or 126 ppm (male rats), 63 or 252 ppm (female rats), or 315 or 1,260 ppm (male and female mice) of calcium cyanamide for 2 years failed to develop tumors that were treatment related at statistically significant levels; however, some of the mice did develop hemangiosarcomas of the circulatory system, lymphomas, and leukemia [ACGIH 1991].

2. *Effects on Humans:* Calcium cyanamide is a primary irritant and sensitizer of the eyes, skin, and mucous membranes. The dust of calcium cyanamide is a primary irritant that can induce skin ulcers and be caustic to the eyes [Clayton and Clayton 1981; NLM 1992]. Skin contact with this substance also causes skin sensitization in approximately 0.5% to 1% of exposed workers [ACGIH 1991]. Inhalation of the dust can cause rhinitis, pharyngitis, laryngitis, and tracheobronchitis. Nasal septal perforation has also been reported in chronically exposed workers. Workers exposed to calcium cyanamide at unspecified concentrations may develop miosis, salivation, lacrimation, and twitching plus a transient vasomotor disturbance that can cause skin and mucous membrane flushing, nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, and low blood pressure; in severe cases, shock, coma, and death may follow [ACGIH 1991; Gosselin et al. 1984; NLM 1992]. Attacks are usually transient, lasting for 30 min to 2 hr, and the ingestion of alcohol may precipitate or intensify this syndrome [Gosselin et al. 1984]. Although an oral dose of 571 mg/kg has proved fatal in humans, the estimated total lethal dose ranges from 20 to 50 grams [NIOSH 1991; NLM 1992]. However, death occurred within 1 hr when a patient drank ethanol following ingestion of 100 mg calcium cyanamide [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium cyanamide can cause eye irritation, runny nose, sore throat, and coughing. Itchy, reddened skin, especially on the exposed areas of the body, has been reported; continued skin contact may cause skin burns. Inhalation exposure can produce respiratory tract irritation and may cause facial and upper-body flushing, accompanied by nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, a sense of oppression in the chest, and shivering. Low blood pressure, circulatory collapse, and coma may follow in more serious exposures. These symptoms may be triggered or intensified by alcohol ingestion, and a marked intolerance to alcoholic beverages can develop.

2. *Chronic exposure:* Calcium cyanamide may cause some individuals to develop skin sensitization, with raised, reddened, and itching areas of the skin (hives). Chronic rhinitis and nasal septal perforation have also been reported in workers exposed to the dust.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! Immediately, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium cyanamide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

   NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium cyanamide and may result in worker exposures to this substance:

—Use in the nitridation and desulfurization of steel

—Use as a raw material in the manufacture of dicyandiamide and calcium cyanide

—Use as a fertilizer and in the manufacture of nitrogen products

—Use in human medicine to treat alcoholism

—Used formerly as a defoliant, herbicide, and pesticide

The following methods are effective in controlling worker exposures to calcium cyanamide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to calcium cyanamide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and on a history of allergies or alcohol intake. All potentially exposed workers should be warned of the adverse signs and symptoms associated with exposure to calcium cyanamide and the concomitant ingestion of alcohol.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium cyanamide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of alcohol intake or allergies and other findings consistent with skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium cyanamide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium cyanamide on the skin (including allergic sensitization) and on any vasomotor episodes that have occurred. All workers should be reminded of the adverse effects associated with concomitant exposure to calcium cyanamide and the ingestion of alcohol. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium cyanamide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium cyanamide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If calcium cyanamide contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with calcium cyanamide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium cyanamide, particularly its potential to cause irritation of the eyes and skin.

A worker who handles calcium cyanamide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium cyanamide or a solution containing calcium cyanamide is handled, processed, or stored.

STORAGE

Calcium cyanamide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium cyanamide should be protected from physical damage and should be stored separately from moisture, calcium carbide, heat, sparks, and open flame. Because containers that formerly contained calcium cyanamide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving calcium cyanamide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Prevent any contact of calcium cyanamide with water.
6. Use nonsparking tools and equipment for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium cyanamide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium cyanamide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of calcium cyanamide per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium cyanamide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium cyanamide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium cyanamide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium cyanamide. Chemically resistant gloves, boots, aprons, and gauntlets are recommended to prevent contact of the skin with this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to permeation by calcium cyanamide. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium cyanamide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium cyanamide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium cyanamide. Contact lenses should not be worn if the potential exists for calcium cyanamide exposure.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM HYDROXIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium hydroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$Ca(OH)_2$

- **Synonyms**

Bell mine, calcium hydrate, hydrated lime, caustic lime, Kemikal, slaked lime

- **Identifiers**

1. CAS No: 1305-62-0
2. RTECS No.: EW2800000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Calcium hydroxide is a soft, white, powder or granule, noncombustible material with a bitter taste and no odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): Decomposes at 580°C (1,076°F)
3. Specific gravity (water = 1): 2.24 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 580°C (1,076°F) (loses its water)
6. Vapor pressure: Not applicable
7. Solubility: Soluble in water, sugar or ammonium solutions, acids, and glycerol; insoluble in alcohol
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Explosions may result from con-

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tact of calcium hydroxide with maleic anhydride, phosphorus, nitroethane, nitromethane, nitroparaffins, or nitropropane.

3. Hazardous decomposition products: Toxic particulates (such as calcium oxide) may be released in a fire involving calcium hydroxide.

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium hydroxide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of irritation associated with exposure to calcium hydroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium hydroxide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium hydroxide is a corrosive that affects all tissues it contacts. Direct application of an aqueous 10% calcium hydroxide solution to the central corneal surface of rabbit eyes resulted in corrosion with persisting severe irritation beyond 21 days [NLM 1992]. The oral LD_{50}s in rats and mice are 7,340 and 7,300 mg/kg, respectively [NIOSH 1991]. The eyes of rabbits were severely affected by the application of 10 mg calcium hydroxide [Grant 1986; Sax and Lewis 1989]. Rats whose drinking water contained 50 or 350 mg calcium hydroxide/liter became restless and aggressive after 2 months and showed a loss in body weight, decreased phagocyte and erythrocyte counts, and decreased hemoglobin after 3 months on this regimen. Autopsy showed inflammation of the small intestines and dystrophic changes in the stomach, kidneys, and liver of these animals [Proctor et al. 1988].

2. *Effects on Humans:* Calcium hydroxide is a tissue corrosive and one of the most common causes of corrosive chemical eye burns. Direct contact of the skin with calcium hydroxide causes skin irritation and may also lead to corrosive chemical burns [Grant 1986; Clayton and Clayton 1981]. Because calcium hydroxide slowly penetrates the skin, the degree of damage is directly related to the degree and duration of exposure [NLM 1992]. Prolonged contact of the skin with calcium hydroxide may cause skin desquamation and a vesicular rash, skin ulceration, and corrosion in some cases [Parmeggiani 1983; NLM 1992]. Ingestion of this material has caused severe pain, vomiting, tissue corrosion, perforation, and death. Survivors may develop esophageal strictures [NLM 1992]. Chronic dermatitis can also be induced by repeated exposure to this alkali [NLM 1992]. Chronic inhalation of calcium hydroxide dust is reported to have caused bronchitis and pneumonia [Parmeggiani 1983].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium hydroxide can induce redness, tearing, irritation, or corrosion of the eyes; runny nose, upper respiratory tract irritation, bronchitis, and pneumonia; and redness, rashes, irritation, or corrosion of the skin.

2. *Chronic exposure:* Calcium hydroxide can cause chronic skin dermatitis, desquamation, vesiculation, and ulceration, as well as coughing, fluid in the lungs, and difficult breathing.

- **Emergency procedure**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash

skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium hydroxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium hydroxide and may result in worker exposures to this substance:

—Manufacture of medicinal antacids, fecal deodorants, polysaccharides, mortar, plaster, whitewash, cement, and other paving and building materials

—Use as an intermediate in the production of propylene oxide and calcium hypochlorite, as a flux in iron and steel manufacture, and as a buffering agent for metals, pearls, and celluloid

—Use in lubricants, drilling fluids, fertilizers, and pesticides

—Use to dehair hides

—Use in water softening and treatment and in water-based paints

—Use in fireproofing compounds, fireproof coatings, and in soil treatment

—Use as a scrubbing and neutralizing agent in the chemical industry

—Manufacture of calcium salts, causticizing soda, and depilatories

—Use in ammonia recovery, in gas manufacture, in paper pulp manufacture, in the purification of sugar juices, as a disinfectant, as an accelerator for low-grade rubber compounds, in petrochemicals, and as a shell-forming agent in the poultry industry

The following methods are effective in controlling worker exposures to calcium hydroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to calcium hydroxide, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium hydroxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium hydroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium hydroxide on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium hydroxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium hydroxide is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 480 liters is collected. The sample is then treated with water to extract the calcium hydroxide. Analysis is conducted by atomic absorption spectroscopy. This method has a sampling and analytical error of 0.28 and is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If calcium hydroxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium hydroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium hydroxide, particularly its potential to cause skin burns.

A worker who handles calcium hydroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium hydroxide or a solution containing calcium hydroxide is handled, processed, or stored.

STORAGE

Calcium hydroxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium hydroxide should be protected from physical damage and should be stored separately from acidic materials, maleic anhydride, nitroethane, nitromethane, nitropropane, nitroparaffins, phosphorus, heat, sparks, and open flame. Because containers that formerly contained calcium hydroxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium hydroxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill to reduce dust concentration.
4. To the extent possible, avoid generating dust during cleanup.
5. For small spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium hydroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium hydroxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium hydroxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium hydroxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium hydroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium hydroxide. Chemically resistant clothing, gloves, boots, and other protective clothing are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by calcium hydroxide and may provide protection for periods greater than 8 hr: natural rubber, nitrile rubber, and neoprene rubber. Polyvinyl chloride has also demonstrated good-to-excellent resistance when tested against calcium hydroxide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium hydroxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium hydroxide. Contact lenses should not be worn if the potential exists for calcium hydroxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

Supplement III–OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
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CONTENTS

REVISED GUIDELINES

NEW GUIDELINES

NOTE TO THE READER

This document is the third in a series of supplements to the 1981 Publication *NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards* (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). The two previous supplements are as follows:

1. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 88-118, Supplement I-OHG). This document contains 35 guidelines.
2. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 89-104, Supplement II-OHG). This document contains 30 guidelines.

The 50 guidelines presented here in the third supplement include 33 revisions of previously issued guidelines and 17 new guidelines. Readers should replace the outdated guidelines in the original 1981 publication with the revised guidelines provided here.

The 50 occupational safety and health guidelines presented here are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes (1) data on the chemical name and synonyms, chemical and physical properties, exposure limits, and signs and symptoms of exposure, and (2) recommendations for medical monitoring, personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers to achieve sound occupational health programs.

The recommendations and information in these guidelines may be superseded as new information becomes available; readers should therefore regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

The first two supplements to the original guidelines can be ordered from the Superintendent of Documents (U.S. Government Printing Office, Washington, DC 20402-9325) or from the National Technical Information Service (5285 Port Royal Road, Springfield, VA 22161 [telephone: 703-487-4650]). The original three-volume set of guidelines is available only from the National Technical Information Service (NTIS). The stock numbers for the U.S. Government Printing Office (GPO) and NTIS are as follows:

Publication	*GPO No.*	*NTIS No.*
Volumes I, II, III (DHHS [NIOSH] Publication No. 81-123)	—	PB 83-154609
Supplement I-OHG (DHHS [NIOSH] Publication No. 88-118)	017-033-00439-1	PB 89-203129
Supplement II-OHG (DHHS [NIOSH] Publication No. 89-104)	017-033-00441-2	PB 89-203137

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM OXIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium oxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CaO

- **Synonyms**

  Lime, burnt lime, calcia, calx, quicklime, pebble lime, unslaked lime

- **Identifiers**

1. CAS No.: 1305-78-8
2. RTECS No.: EW3100000
3. DOT UN: 1910 60
4. DOT label: None

- **Appearance and odor**

  Calcium oxide may take the form of odorless crystals, white or grayish-white lumps, or granular powder. The commercial material may have a yellowish or brownish tint because of its iron content.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 56.08
2. Boiling point (760 mm Hg): 2,850°C (5,162°F)
3. Specific gravity (water = 1): 3.32 to 3.35 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 2,572°C (4,662°F)
6. Vapor pressure at 20°C (68°F): 0 mm Hg
7. Solubility: Soluble in water (forms slaked lime and generates a large quantity of heat); soluble in acids, glycerol, and sugar solution; practically insoluble in alcohol.
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Moisture

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2. Incompatibilities: Contact of calcium oxide with water causes a violent reaction, and the heat liberated during this reaction may cause the ignition of combustible substances. Calcium oxide reacts violently with ethanol, liquid hydrogen fluoride, some acids, some halogens, some metal halides, some metals, and some oxides, boron trifluoride, liquid hydrofluoric acid, phosphorus pentoxide, boric oxide and calcium chloride mixtures, fluorine, chlorine trifluoride, and carbon dioxide.

3. Hazardous decomposition products: Toxic particulates (such as particles of calcium hydroxide) may be released in a fire involving calcium oxide.

4. Special precautions: When exposed to air, this substance will react with the moisture and the carbon dioxide in the air. Calcium oxide swells when moist and may burst its containers.

Flammability

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) for calcium oxide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Calcium oxide will not burn. Because water reacts violently with calcium oxide, it should NOT be used as an extinguishant. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium oxide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium oxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do NOT allow water to come into contact with the contents of containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium oxide. Structural firefighters' protective clothing may provide limited protection against fires involving calcium oxide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium oxide is 5 mg/m^3 as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium oxide a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of eye, skin, and respiratory tract irritation associated with exposure to calcium oxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium oxide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* No published data on the effects of calcium oxide exposure in animals were available for review.

2. *Effects on Humans:* Calcium oxide causes marked irritation and corrosion of contacted tissues. The irritant and corrosive effects of exposure to calcium oxide dust are primarily a result of its alkalinity and

its heat-generating reaction when in contact with moisture [Clayton and Clayton 1981]. Addition of water to calcium oxide has generated temperatures as high as 800°C (1,472°F) [NLM 1991]. In contact with the eyes, calcium oxide causes severe burns and may cause corneal ulceration [Grant 1986; Sittig 1985]. In contact with the skin, calcium oxide causes dermatitis or corrosive burns, with desquamation and a vesicular rash [Sittig 1985]. Inhalation of the dust at a concentration of 25 mg/m^3 caused marked nasal irritation in exposed workers; however, at a concentration of 9 or 10 mg/m^3, this effect disappeared [Clayton and Clayton 1981]. Exposure to calcium oxide at unspecified concentrations causes inflammation of the respiratory passages and ulceration and perforation of the nasal septum [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium oxide can produce spasmodic blinking, tears, and adhesion of calcium oxide particles to the eyeball and the conjunctival sac; dermatitis with desquamation and a vesicular rash, ulceration, and corrosive burns; and coughing, sneezing, and inflammation of the nose and throat, bronchitis, and pneumonia.

2. *Chronic exposure:* Calcium oxide has caused ulceration and perforation of the nasal septum and severe recurrent dermatitis.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium oxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium oxide and may result in worker exposures to this substance:

—Use as raw material in the preparation of chlorinated lime, bleaching powder, and calcium salts and as a binding agent in the manufacture of Portland cement, mortar, stucco, plaster, bricks, refractory material, and glass

—Use as a softening, purifying, coagulating, and suspending compound in water treatment and purification; as a neutralizer of acid waste effluents; to remove sulfur dioxide from stack gases; to treat sewage and waste from steel fabrication and chemical, pharmaceutical, and explosives manufacturing facilities; and to remove sulfur from process streams in petroleum refining

—Use in wire-drawing operation in the manufacture of iron and steel; as a promoter of iron catalysts in ammonia synthesis; in flotation of nonferrous ores and in the refining of ores to remove silica; and as a flux during metal refining and smelting

—Manufacture of aluminum, magnesium, calcium carbide, and sodium carbonate and in the synthesis of chemical and dye intermediates, paint pigments, pharmaceuticals, drilling fluids, and lubricants

—Use in Kraft pulp processing of paper, to clarify cane and beet sugar juices, and as a nutrient and/or dietary supplement and food additive

—Use in dehairing of hides in leather manufacture; in manufacture of pesticides, insecticides, and fungicides; and in cleaning operations as bleach, disinfectant, and deodorizer

The following methods are effective in controlling worker exposures to calcium oxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium oxide, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium oxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium oxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium oxide on the eyes (especially the cornea and conjunctiva), skin, and respiratory tract. The mucosa of the nose and mouth and the nasal septum should be examined for evidence of ulceration or perforation. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium oxide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium oxide is determined by using a 0.8-micron mixed cellulose ester filter (MCEF). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 400 liters is collected. The samples are ashed with nitric and hydrochloric acids. Ionization interferences are controlled with 1,000 µg/ml potassium. Analysis is conducted by atomic absorption spectroscopy with a nitrous oxide/acetylene flame. The limit of detection for this procedure is 0.03 µg/ml. This method is described in OSHA Method No. ID-121 in the *OSHA Analytical Methods Manual* [OSHA 1985]. A similar method is described in NIOSH Method 7020 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If calcium oxide contacts the skin, particles should be removed with oil or grease before they are flushed with flooding amounts of water.

Clothing contaminated with calcium oxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium oxide, particularly its potential to cause eye, skin, and upper respiratory tract irritation and burns.

A worker who handles calcium oxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium oxide or a solution containing calcium oxide is handled, processed, or stored.

STORAGE

Calcium oxide should be stored in a cool, dry, well-ventilated area in tightly sealed, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium oxide should be protected from physical damage and should be stored separately from water and other sources of moisture, acids, oxidizers, organic materials, other combustibles, heat, and open flame. Because containers that formerly contained calcium oxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium oxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be followed after a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of moisture.
4. Ventilate the area of the spill.
5. Do NOT use water on the spilled material; collect the spilled material and gently place it in a clean, dry container creating as little dust as possible. Cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium oxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium oxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium oxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium oxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium oxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, gauntlets, and coveralls) should be worn to prevent any skin contact with calcium oxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium oxide permeation; however, natural rubber, neoprene, and nitrile rubber have been tested against chemically similar materials (calcium hydroxide) and may provide protection for more than 8 hr. Since specific data are not available for calcium oxide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium oxide.

Goggles or face shields should be worn during operations in which calcium oxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium oxide. Contact lenses should not be worn if the potential exists for calcium oxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM SILICATE

INTRODUCTION

This guideline summarizes pertinent information about calcium silicate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaSiO_3$

- **Synonyms**

  Calcium metasilicate, wollastonite, calcium hydrosilicate, calcium monosilicate, calcium salt of silicic acid, Calflo E, Calsil, CS Lafarge, Micro-Cel, Silene EF

- **Identifiers**

  1. CAS No.: 1344-95-2
  2. RTECS No.: VV9150000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium silicate is a noncombustible, white or cream-colored, free-flowing powder that is prepared commercially from lime and diatomaceous earth; many different calcium silicates occur in nature in mineral form (e.g., wollastonite, afwillite, grammite).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 116.16
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity (water = 1): 2.9 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: 1,540°C (2,804°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; forms a siliceous gel with mineral acids
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: None reported

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: None reported

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium silicate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium silicate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium silicate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium silicate is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable dust) for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium silicate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on calcium silicate's local irritant properties.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium silicate can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* The toxicity of calcium silicate depends on the silica content and amount of respirable fiber in the particular calcium silicate preparation; studies in animals should be interpreted with this information in mind. Rats exposed to 10 mg/m^3 concentrations of various calcium silicate preparations, measured as respirable dust (approximately 19 to 25 mg/m^3 total dust), for 7 hr/day, 5 days/week for 224 days in a 12-month period showed no pulmonary lesions except for a few nodules in the animals exposed to the calcium silicate preparation that contained about 1% crystalline silica [ACGIH 1991]. No mesotheliomas were seen in groups of rats injected intraperitoneally with three different calcium silicate preparations [ACGIH 1991]. One experiment in rats showed a significant increase in the incidence of pleural sarcomas after wollastonite (naturally occurring calcium silicate) fibers were implanted intrapleurally [IARC 1987]. Rats, guinea pigs, and hamsters exposed for as long as 36 months to synthetic calcium silicate containing 15% asbestos at concentrations ranging from 100 to 125 million particles per cubic foot (mppcf) developed fibrosis; the authors of this study attributed the fibrosis to the asbestos in the product [ACGIH 1991].

2. *Effects on Humans:* The toxicity of calcium silicate depends on the particle size, amount of silica, the aspect ratio, and the amount of respirable fiber in the particular calcium silicate product being used; studies in humans should be interpreted with this in mind. Calcium silicate causes physical irritation when in contact with the eyes, skin, or upper respiratory tract of exposed workers. In vitro toxicity studies of calcium silicate insulation materials demonstrated equivocal hemolysis potential (one greater versus one less)

but less cytotoxicity than asbestos [ACGIH 1991]. A 23-year-old warehouse worker developed a skin reaction to calcium silicate after 3 days of exposure to an atmosphere described only as permeated with the silicate. The skin condition was characterized by patches of itchy, erythematous papular eruptions that cleared after work [Lachapelle 1984]. A study of 104 U.S. wollastonite workers with more than 1 year of exposure (mean duration of exposure approximately 9.2 years) showed no relationship between the prevalence of chronic bronchitis, airflow obstruction, or abnormal diffusing capacity in workers with increasing exposure to wollastonite [Rom 1983].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to calcium silicate include pain and redness of the eyes; itching, redness, and eruptions of the skin; and scratchiness of the throat.
2. *Chronic exposure:* Synthetic or natural materials that have calcium silicate as a base may cause dermal irritation after prolonged contact and possible induction of altered pulmonary function and lesions when silica or asbestos are also present.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.
2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.
3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.
4. *Ingestion exposure:* Take the following steps if calcium silicate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.
5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve calcium silicate and may result in worker exposures to this substance:

—Use as a substitute for materials containing silica in ceramics and as a substitute for asbestos in wallboard, insulation, and brake linings

—Use as a constituent of lime glass and Portland cement

—Use as a reinforcing filler in elastomers and plastics, paints, ceramics, paper, and wallboard

—Use as an anticaking ingredient in table salt, baking powder, foods, powdered pharmaceuticals, and cosmetics

—Use as an aggregate in road construction

—Use as a binder in refractory material, as a thermal insulator, and as a paper coating in chromatography

—Use as a veterinary antacid and absorbent

—Use as a carrier in the formulation of triazine herbicides and to provide free-flowing dust for toxic powders such as ground sulfur

The following methods are effective in controlling worker exposures to calcium silicate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium silicate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium silicate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium silicate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium silicate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium silicate.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne concentrations of calcium silicate (total dust) is determined by using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filters. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System under Dust (total) [OSHA 1989]. NIOSH has a similar method (Method 0500) that also involves gravimetric analysis [NIOSH 1984a]. The sample flow rate in the NIOSH method is between 1.5 and 2.0 liters/min. The minimum volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum sample volume at 15 mg/m^3 is 133 liters. The overall precision of the NIOSH method is 0.056.

A worker's exposure to airborne concentrations of calcium silicate (respirable fraction) is determined by using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is held in a 10-mm nylon cyclone, at a flow rate of 1.7 liter per minute until a maximum air volume of 800 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filters. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System under Dust (Respirable Nuisance) [OSHA 1989]. NIOSH has a similar method (Method 0600) that also involves gravimetric analysis [NIOSH 1984b]. The sample flow rate in the NIOSH method is 1.7 liter/min. The minimum volume for an airborne concentration of 5 mg/m^3 is 75 liters and the maximum sample volume at 5 mg/m^3 is 1,000 liters. The overall precision of the NIOSH method ranges from 0.043 on laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium silicate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium silicate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium silicate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cometics in areas where calcium silicate is handled, processed, or stored.

STORAGE

Calcium silicate should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of calcium silicate should be protected from physical damage. Because containers that formerly contained calcium silicate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium silicate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Use a wet method, a scoop, or a vacuum to clean up this material.
2. Place the material into a clean, dry container.
3. Cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium silicate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium silicate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium silicate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium silicate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium silicate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with calcium silicate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions for use. No reports have been published on the resistance of various protective clothing materials to calcium silicate permeation. If permeability data are not available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium silicate.

If calcium silicate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium silicate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium silicate. Contact lenses should not be worn if the potential exists for calcium silicate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM SULFATE

INTRODUCTION

This guideline summarizes pertinent information about calcium sulfate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaSO_4$

- **Synonyms**

  Anhydrous calcium sulfate; anhydrous gypsum; anhydrous sulfate of lime; crysalba; dead-burned gypsum; drierite; gibs; karstenite; muriacite; natural anhydrite; sulfuric acid, calcium salt; thiolite

- **Identifiers**

  1. CAS No.: 7778-18-9
  2. RTECS No.: WS6920000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium sulfate is an odorless, noncombustible solid. The natural form of anhydrous calcium sulfate is known as the mineral anhydrite consisting of crystals or granules of varying color (e.g., white with a blue, gray, or reddish tinge or brick red). Insoluble anhydrite, which has the same crystal structure as the mineral, is obtained upon complete dehydration of gypsum at above 650°C. Soluble anhydrite is obtained in granular or powder form by complete dehydration of gypsum at or below 300°C in an electric oven.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 136.14
  2. Boiling point (760 mm Hg): 1,193°C (2,179.4°F)
  3. Specific gravity (water = 1): 2.96 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 1,450°C (2,642°F)
  6. Vapor pressure at 20°C (68°F): Not applicable
  7. Solubility: Anhydrous calcium sulfate is insoluble in water but soluble in acid, ammonium salts, sodium thiosulfate, and glycerin.
  8. Evaporation rate: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: None reported

2. Incompatibilities: Explosions may result from contact of calcium sulfate with diazomethane, aluminum, or phosphorus.

3. Hazardous decomposition products: Toxic gases and particulates (such as oxides of sulfur) may be released in a fire involving calcium sulfate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium sulfate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Calcium sulfate will not burn. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium sulfate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium sulfate.

XPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium sulfate is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium sulfate (total dust) a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to calcium sulfate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium sulfate can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* There is no acute information on the effects of calcium sulfate exposure in experimental animals. A month-long exposure study in animals (undefined species, route, and doses) induced bronchitis and interstitial pneumonia while exposure for 9 months caused pulmonary changes resembling those found for pneumosclerosis [Voropaev 1967]. Female rats that received four 25-mg intraperitoneal injections of calcium sulfate (gypsum) showed a slight increase in cancer rates when compared to the controls 5.7% and 0%, respectively. Mean survival rates were similar 587 days for gypsum and 592 days for controls [Pott et al. 1976].

2. *Effects on Humans:* Calcium sulfate causes irritation of the eyes, skin, mucous membranes, and upper respiratory tract in humans. Conjunctivitis, rhinitis, laryngitis, sore throat, tracheal and bronchial irritation, nosebleeds, and impaired sense of smell and taste have been reported in workers exposed to this substance [Parmeggiani 1983; Genium 1990; NLM 1991]. Although chronic lung disease has not been reported among domestic calcium sulfate workers [ACGIH 1991], a Russian paper reported that unfavorable ambient dust loads among female workers in

the gypsum industry caused increased incidences of alveolar modular fibrosis, subatrophic rhinitis, laryngitis, and pharyngitis [Voropaev 1967]. It is unclear whether the gypsum processed in Russia also contained other lung toxicants such as quartz [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to calcium sulfate can cause redness and itching of the eyes, runny nose, sore throat, and irritation of the respiratory tract and skin.

2. *Chronic exposure:* Calcium sulfate is a mucous membrane irritant that can also affect the eyes, impair the sense of smell and taste, and can cause nosebleeds. It may also cause pulmonary nodular fibrosis.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium sulfate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium sulfate and may result in worker exposures to this substance:

—Manufacture of phosphoric acid from phosphate rock

—Use as a drying agent for solids, organic liquids, and gases

—Use as a chemical intermediate in the manufacture of sulfuric acid and as a reagent in the laboratory detection of aflatoxins

—Use in the manufacture of tofu and as a dietary source of calcium in poultry

—Use as a food additive in canned vegetables, bakery products, cheeses, and as a bleaching agent in flour

—Use as an ingredient in a copper poisoning antidote in sheep

—Use as a paper filler and a component of cement

The following methods are effective in controlling worker exposures to calcium sulfate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium sulfate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium sulfate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium sulfate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium silicate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium silicate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

OSHA's method for the determination of worker exposure to airborne concentrations of calcium sulfate (total dust) is made by using a tared, low-ash polyvinyl chloride filter with a 5 micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Dust, Total [OSHA 1987]. NIOSH has a similar method (Method 0500), which also involves gravimetric analysis [NIOSH 1984a]. The sample flow rate in the NIOSH method is between 1.5 and 2.0 liters/min. The minimum sample volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum sample volume is 133 liters. The overall precision for the NIOSH method is 0.056.

OSHA's method for the determination of worker exposure to airborne concentrations of calcium sulfate (respirable fraction) is made by using a tared, low-ash polyvinyl chloride filter with a 5 micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is preceded by a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Dust (Respirable Nuisance) [OSHA 1987]. NIOSH has a similar method (Method 0600), which also involves gravimetric analysis [NIOSH 1984b]. The sample flow rate in the NIOSH method is 1.7 liter/min. The minimum sample volume for an airborne concentration of 5 mg/m^3 is 75 liters, and the maximum sample volume is 1,000 liters. The overall precision for the NIOSH method ranges from 0.043 to 0.145 in laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium sulfate contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with calcium sulfate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium sulfate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium sulfate is handled, processed, or stored.

STORAGE

Calcium sulfate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium sulfate should be protected from physical damage and should be stored separately from aluminum, diazomethane, phosphorus, heat, sparks, and open flame. Because containers that formerly contained calcium sulfate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium sulfate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Avoid dust generation and remove all sources of heat and ignition.

2. Ventilate the area of the spill.

3. Use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Calcium sulfate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium sulfate; there is no reportable quantity for this substance.

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Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium sulfate emitted or released from their facility annually.

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Parmeggiani L [1983]. Encyclopedia of occupational health and safety. 3rd rev. ed. Geneva, Switzerland: International Labour Organisation.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

Supplement IV-OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Cincinnati, Ohio

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CONTENTS

REVISED GUIDELINES

NEW GUIDELINES

NOTE TO THE READER

This document is the fourth in a series of supplements to the 1981 Publication *NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards* (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). The three previous supplements are as follows:

1. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 88-118, Supplement I-OHG). This document contains 35 guidelines.
2. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 89-104, Supplement II-OHG). This document contains 30 guidelines.
3. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 92-110, Supplement III-OHG). This document contains 50 guidelines.

The 62 guidelines presented here in the fourth supplement include 11 revisions of previously issued guidelines and 51 new guidelines. Readers should replace the outdated guidelines in the original 1981 publication with the revised guidelines provided here.

The 62 occupational safety and health guidelines presented here are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes (1) data on the chemical name and synoyms, cemnical and physical properties, exposure limits, and signs and symptoms of exposure, and (2) recommendations for medical monitoring, personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers to achieve sound occupational health programs.

The recommendations and information in these guidelines may be superseded as new information becomes available; readers should therefore regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

The original three-volume set of guidelines and the first three supplements to the original guidelines are available through the National Technical Information Service (NTIS) (5285 Port Royal Road, Springfield, VA 22161 [telephone: 703-487-4650]). The third suuplement can also be ordered from the Superintendent of Documents (U.S. Government Printing Office, Washington, DC 20402-9325). The stock numbers for the U.S. Government Printing Office (GPO) and NTIS are as follows:

Publication	*GPO No.*	*NTIS No.*
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Supplement III-OHG (DHHS [NIOSH] Publication No. 92-110)	017-033-00464-1	PB 93-183903

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAMPHOR, SYNTHETIC

INTRODUCTION

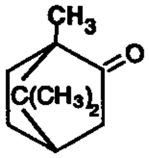
This guideline summarizes pertinent information about synthetic camphor for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{16}O$

- **Structure**



- **Synonyms**

2-Camphanone, 2-bornanone, gum camphor, Formosa camphor, Japan camphor, matricaria camphor, 1,7,7-trimethylbicyclo(2.2.1)-2-heptanone, laurel camphor, 2-keto-1,7,7-trimethylnorcamphane

- **Identifiers**

1. CAS No.: 76-22-2
2. RTECS No.: EX1225000
3. DOT UN: 2717 32
4. DOT label: Flammable Solid

- **Appearance and odor**

Camphor is a colorless or white crystalline mass with a penetrating, aromatic odor and slightly bitter, cooling taste. The odor threshold of camphor is reported to be 0.079 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 152.23
2. Boiling point (760 mm Hg): 204°C (399.2°F) sublimes
3. Specific gravity (water = 1): 0.99 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of camphor): 5.2
5. Melting point: 179.8°C (355°F)
6. Vapor pressure at 20°C (68°F): 0.18 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; soluble in aniline, nitrobenzene, carbon disulfide, tetralin, decalin, methylhexalin, petroleum ether, the higher alcohols, and fixed and volatile oils. Also soluble in concentrated mineral acids in phenol, liquid ammonia, and liquid sulfur dioxide.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of camphor with strong oxidizing agents such as potassium permanganate and chromic anhydride may form explosive mixtures.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving camphor.

4. Special precautions: None

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) for camphor.

1. Flash point: 66°C (150°F) (closed cup)

2. Autoignition temperature: 466°C (871°F)

3. Flammable limits in air (% by volume): Lower, 0.6; upper, 3.5

4. Extinguishant: Use dry chemical, sand, water spray, fog, or standard foam to fight fires involving camphor. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving camphor should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of camphor may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving camphor. Structural firefighters' protective clothing may provide limited protection against fires involving camphor.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for camphor is 2 mg/m^3 (approximately 0.3 ppm) of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for camphor of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned camphor a threshold limit value (TLV) of 2 ppm (12 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 3 ppm (19 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 min [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of irritation associated with exposure to camphor.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to camphor can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Camphor is a central nervous system toxin in animals. The toxicity can vary depending on whether the racemate or isomers were studied: *dl*, *d*, *l*, or β [NIOSH 1991]. The lethal concentration for mice exposed to camphor for 3 hr ranged from 400 to 1,760 mg/m^3 [Izmerov et al. 1982]. Although camphor is only slowly absorbed from subcutaneous or intramuscular injection sites, absorption from mucous membranes and alimentary tract is rapid [NLM 1991]. The lowest lethal dose by subcutaneous administration in the mouse is 2,200 mg/kg while the lowest lethal oral dose in rabbits is 2 g/kg [NIOSH 1991]. Animals acutely poisoned may exhibit mydriasis, convulsions, and central nervous system stimulation before death [NIOSH 1991]. Death by asphyxiation occurred in dogs that ingested a lethal amount (9 to 14 g) [NLM 1991]. Prolonged (duration not specified) inhalation of camphor at a concentration of 6 mg/m^3 caused injury described as severe to experimental animals; at autopsy, congestion and edema of the gastrointestinal tract, kidneys, and brain were seen [ACGIH 1991]. Subcutaneous injection of camphor in rats over an 18-month period caused no increase in the incidence of tumors, but the addition of croton oil (a known cancer promoter) to the camphor mixture caused carcinomas in 2 of 110 treated mice [ACGIH 1991].

2. *Effects on Humans:* Camphor is irritating to the nose and throat of exposed individuals; at high concentrations, it is a central nervous system stimulant and convulsant [Proctor et al. 1988]. One fatal case of camphor poisoning discussed in the literature resulted from inhalation of the vapor of heated camphor. In this case, the major symptom of overexposure was marked rigidity of the jaw muscles [ACGIH 1991]. Adults have survived ingested doses up to 1.5 grams while doses of <1 gram have been fatal. A fetal death resulted when a pregnant mother ingested camphor. Necropsy revealed severe atelectasis and central neuronal necrosis in the fetus [NLM 1991]. Serious acute overexposures to unspecified concentrations or ingested amounts can cause irritation, anxiety, headache, nausea, vomiting, excitement, restlessness, dyspnea, dizziness, confusion, delerium, hallucinations, tremors, twitching of facial muscles, spasticity, convulsions, and coma [Proctor et al. 1988; ACGIH 1991]. Death can result from respiratory failure or status epilepticus [NLM 1991]. A study of workers employed in a synthetic camphor packaging plant revealed that daily exposure (5 days/week for up to 10 months) did not cause irritation of the eyes and nose or loss of the sense of smell if the camphor concentration was maintained at or below 2 ppm [ACGIH 1991]. At this or higher concentrations, however, exposure caused eye and nose irritation and loss of the ability to smell [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Camphor can cause irritation of the eyes, nose, and upper respiratory tract; anxiety; headaches; nausea; vomiting; excitement; restlessness; dyspnea; confusion; dizziness; twitching of facial muscles; spasticity; convulsions; and coma.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to camphor include irritation of the eyes and nose and loss of the sense of smell.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if camphor or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of the possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve camphor and may result in worker exposures to this substance:

—Mixing and packaging of cellulose nitrate for photographic film, cosmetics (perfumes), embalming fluid, pharmaceuticals, insect repellants, and mildew repellants

—Manufacture of plastics (especially celluloids), explosives, and incense

—Use as a plasticizer for cellulose esters and ethers, as a preservative in pharmaceuticals and cosmetics, in liniments for lumbago and related disorders, as a respiratory and circulatory stimulant, and as a topical anti-infective, counter-irritant antipruritic, and anesthetic

—Use as a catalyst or chemical intermediate in manufacturing of cumene and sulfuryl chloride, in mixing and blending of certain lacquers and varnishes, and as an odorant-flavorant during preparation and packaging of certain foods, toothpaste and powders, depilatories, deodorants, and tobacco

—Use in dentistry for the treatment of infected root canals

The following methods are effective in controlling worker exposures to camphor, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1991]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to camphor, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to camphor at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with convulsive disorders or diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to camphor exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of camphor on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for camphor.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne camphor is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 25 liters is collected. The samples are desorbed with carbon disulfide methanol (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.05 mg per sample. This method is described in NIOSH Method No. 1301, *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If camphor contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with camphor should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of camphor, particularly its potential to be an irritant of the eyes, respiratory tract, and skin.

A worker who handles camphor should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where camphor or a solution containing camphor is handled, processed, or stored.

STORAGE

Camphor should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard

[29 CFR 1910.1200]. Containers of camphor should be protected from physical damage and should be stored separately from potassium permanganate, chromic anhydride, other oxidizers, heat, sparks, and open flame. Because containers that formerly contained camphor may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving camphor, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Cover area of the spill with dry sand, vermiculite, or other noncombustible absorbent material, mix well, and place into closed containers for later disposal. Keep container tightly sealed.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) regulatory requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Camphor is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of camphor; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of camphor emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although camphor is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 CFR 355.40], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information on their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of camphor exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with camphor. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to camphor permeation, although some sources recommend the use of rubber. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to camphor.

If camphor is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which camphor might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with camphor. Contact lenses should not be worn if the potential exists for camphor exposure.

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NIOSH [1991]. Registry of toxic effects of chemical substances database: camphor, synthetic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPROLACTAM DUST

INTRODUCTION

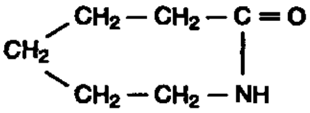
This guideline summarizes pertinent information about caprolactam dust for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NO$

- **Structure**



- **Synonyms**

Aminocaproic lactam; epsilon-caprolactam; 2-oxohexamethylenimine; 2-ketohexamethylenimine; 2-perhydroazepinone; Akulon; Alkamid; Amilan; ATM 2(Nylon); Bonamid; Capran 80; Caprolon B; Capron; Chemlon; Danamid; Durethan BK; Grilon; Itamid; Kaprolit; Maranyl; Miramid; Orgamide; Nylon X 1051; Plaskin 8200; Spencer 401; Tarlon XB; Ultramid; Vidlon

- **Identifiers (For caprolactam)**

1. CAS No.: 105-60-2
2. RTECS No.: CM3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Caprolactam dust is a white, crystalline, finely divided particulate that has an unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES (For caprolactam)

- **Physical data**

1. Molecular weight: 113.2
2. Boiling point (760 mm Hg): 266.9°C (512.42°F)
3. Specific gravity (water = 1): 1.02 at 75°C (167°F)
4. Vapor density (air = 1 at boiling point of caprolactam dust): 3.9
5. Melting point: 70°C (158°F)
6. Vapor pressure at 20°C (68°F): 0.001 mm Hg
7. Solubility: Soluble in water, benzene, chloroform, chlorinated hydrocarbons, cyclohexene, and petroleum fractions; freely soluble in methanol, ethanol, tetrahydrofurfuryl alcohol, ether, and dimethylformamide

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8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Moisture, heat, sparks, and open flame

2. Incompatibilities: Contact of caprolactam dust with strong oxidizing agents should be avoided.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving caprolactam dust.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to caprolactam; other sources rate caprolactam's fire hazard as slight.

1. Flash point: 125°C (257°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 1.84; upper, 8.0

4. Extinguishant: Use carbon dioxide, dry chemical, alcohol foam, or water fog to fight fires involving caprolactam dust. Water or foam may cause frothing. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be used to cool fire-exposed containers.

Fires involving caprolactum dust should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving caprolactam dust.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for caprolactam dust [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 3 mg/m^3 as a STEL. A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned caprolactam dust a threshold limit value (TLV) of 1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 3 mg/m^3 for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of convulsions, dermal sensitization, and dermal and respiratory irritation [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to caprolactam dust can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, caprolactam dust is an irritant of the eyes, nose, and skin and a central nervous system depressant. Applied to the eyes of rabbits, 20 mg of this substance caused a moderate degree of irritation; 500 mg of caprolactam applied to the skin of rabbits for 24 hr caused mild skin irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 1.4 g/kg [NIOSH 1993]. Acutely poisoned animals convulsed and showed other nervous system effects before death [NIOSH 1993]. The oral LD_{50} in rats is 1.2 g/kg; the LC_{50} in the same species is 300 mg/m^3 for 2 hr [NIOSH 1993]. Administered intraperitoneally, caprolactam at doses of 350 to 600 mg/kg caused tremor, convulsions, and a bloody eye discharge [Hathaway et al. 1991]. Guinea pigs tolerated seven daily 7-hr exposures to a concentration of caprolactam ranging from 118 to 261 mg/m^3 without

evidence of adverse effects other than occasional coughing [ACGIH 1991]. Male rats exposed 4 hr/day to a 125 mg/m^3 concentration of caprolactam dust for 2.5 months showed increasing excitability, changes in spermatogenesis, and a decrease in respiratory rate and urinary function [IARC 1986]. Exposure to a 11 mg/m^3 concentration on the same regimen caused no adverse reproductive effects [IARC 1986]. In a 3-generation reproductive study in rats fed caprolactam at a dietary dose of 5,000 or 10,000 ppm, this substance caused dose-related decreases in food consumption and in body weight in dams and pups; at a dietary level of 10,000 ppm, signs of minimal kidney toxicity were seen in males at autopsy, but no reproductive or fetotoxic effects were observed [ACGIH 1991]. A 2-year carcinogenicity bioassay of caprolactam in mice and rats showed negative results [IARC 1986].

2. *Effects on Humans:* In humans, exposure to caprolactam causes eye, skin, and respiratory tract irritation, convulsions, and, in some individuals, dermal sensitization [ACGIH 1991]. Repeated exposure of the skin to the dust of caprolactam causes peeling and fissuring in chronically exposed workers [ACGIH 1991]. Workers exposed to the fumes of caprolactam (condensed from the vapor) at concentrations ranging from 6 to 131 mg/m^3 for 9 months to 13 years reported sensory irritation and dermatitis; however, no caprolactam-related pulmonary effects or signs of systemic toxicity were seen in these workers [ACGIH 1991]. Another study showed that workers repeatedly exposed to caprolactam dust (condensed vapor) generated by the spinning process complained of a bitter taste, nervousness, nose bleeds, productive cough, and dry, split mucous membranes. Some complained of flatulence, heartburn, and a heavy feeling in the stomach [ACGIH 1991]. A group of male workers exposed to several chemicals, including caprolactam dust, showed an increase in sperm abnormalities, and women occupationally exposed to this substance have been reported to have an increased rate of complications during pregnancy; however, confounding exposures and other methodological problems make interpretation of these results difficult [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to caprolactam dust may cause redness, inflammation, and tearing of the eyes; redness and inflammation of the eyelids; runny nose; scratchy throat; coughing; and redness or blistering of the skin.

2. *Chronic exposure:* Chronic exposure to caprolactam dust may cause dermatitis (fissuring, peeling, and inflammation); some individuals become sensitized to caprolactam and may have an allergic skin reaction (i.e., hives) to this substance on subsequent exposure.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if caprolactam dust or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and procedures for protecting themselves in rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve caprolactam dust and may result in worker exposures to this substance:

—Use as a chemical intermediate in the production of nylon-6 fibers and plastics

—Use as a solvent for some high molecular weight polymers

—Use in making coatings, plasticizers, paint vehicles, and synthetic leather

The following methods are effective in controlling worker exposures to caprolactam dust, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to caprolactam dust, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to caprolactam dust at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, and respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to caprolactam dust exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of caprolactam dust on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for caprolactam dust.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne caprolactam dust is determined by using an OSHA Versatile Sampler (OVS-7), 13-mm XAD-7 tube (270/140-mg sections, 20/60 mesh), with a glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 100 liters (TWA) or 15 liters (STEL) is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If caprolactam dust contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with caprolactam dust should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of caprolactam dust.

A worker who handles caprolactam dust should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where caprolactam dust is present.

STORAGE

Caprolactam should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical equipment in use in storage areas should be of explosionproof design. Carrying equipment and storage containers should be grounded and bonded to prevent a dust explosion, and bulk storage systems should have an explosion-relief design. Containers of caprolactam dust should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained caprolactam dust may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving caprolactam dust, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Cover spill with sand, vermiculite, or soda ash and place material into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Caprolactam is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center about an accidental release of caprolactam dust; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of caprolactam dust emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although caprolactam dust is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of caprolactam dust exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.1200]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with caprolactam dust. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to caprolactam dust permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to caprolactam dust.

If caprolactam dust is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which caprolactam dust might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with caprolactam dust. Contact lenses should not be worn if the potential exists for caprolactam dust exposure.

REFERENCES CITED

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NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

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NIOSH [1993]. Registry of toxic effects of chemical substances database: caprolactam. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPROLACTAM VAPOR

INTRODUCTION

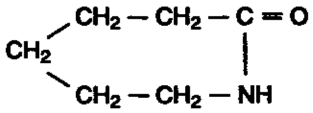
This guideline summarizes pertinent information about caprolactam vapor for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NO$

- **Structure**



- **Synonyms**

Aminocaproic lactam; epsilon-caprolactam; 2-oxohexamethylenimine; 2-ketohexamethylenimine; 2-perhydroazepinone; Akulon; Alkamid; Amilan; ATM-2 (Nylon); Bonamid; Capran 80; Caprolon B; Capron; Chemlon; Danamid; Durethan BK; Grilon; Itamid; Kaprolit; Maranyl; Miramid; Orgamide; Nylon X 1051; Plaskin 8200; Spencer 401; Tarlon XB; Ultramid; Vidlon

- **Identifiers (For caprolactam)**

1. CAS No.: 105-60-2
2. RTECS No.: CM3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Caprolactam vapor is caprolactam in the vapor state. The vapor evolves only at high temperatures, because the vapor pressure of caprolactam is low. Caprolactam vapor is colorless and has an unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES

(For caprolactam)

- **Physical data**

1. Molecular weight: 113.2
2. Boiling point (760 mm Hg): 266.9°C (512.42°F)
3. Specific gravity (water = 1): 1.02 at 75°C (167°F)
4. Vapor density (air = 1 at boiling point of caprolactam vapor): 3.9
5. Melting point: 70°C (158°F)
6. Vapor pressure at 20°C (682°F): 0.001 mm Hg

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7. Solubility: Soluble in water, benzene, chloroform, chlorinated hydrocarbons, cyclohexene, and petroleum fractions; freely soluble in methanol, ethanol, tetrahydrofurfuryl alcohol, ether, and dimethylformamide

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Moisture, heat, sparks, and open flame

2. Incompatibilities: Contact of caprolactam vapor with strong oxidizing agents should be avoided.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving caprolactam vapor.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to caprolactam vapor; other sources rate caprolactam's fire hazard as slight.

1. Flash point: 125°C (257°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 1.84; upper, 8.0

4. Extinguishant: Use carbon dioxide, dry chemical, alcohol foam, or water fog to fight fires involving caprolactam vapors. Water or foam may cause frothing. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be used to cool fire-exposed containers.

Fires involving caprolactam vapors should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving caprolactam vapor.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for caprolactam vapor [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.22 ppm (1 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.66 ppm (3 mg/m^3) as a STEL. A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned caprolactam vapor a threshold limit value (TLV) of 5 ppm (23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 10 ppm (46 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of convulsions, dermal and respiratory irritation, and dermal sensitization [NIOSH 1992]; the ACGIH limits are based on the risk of eye, skin, and upper respiratory tract irritation associated with exposure to caprolactam vapor [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to caprolactam vapor can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, caprolactam vapor is an irritant of the eyes, upper respiratory tract, and skin and a central nervous system depressant. Applied to the skin of rabbits for 24 hr, 500 mg of caprolactam caused mild skin irritation; instilled into the eyes of rabbits, 20 mg of this substance caused a moderate degree of irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 1.4 g/kg [NIOSH 1993]. Acutely poisoned animals convulsed and showed other nervous system effects before death [NIOSH

1993]. The oral LD_{50} for caprolactam in rats is 1.2 g/kg; the LC_{50} in the same species is 300 mg/m^3 for 2 hr [NIOSH 1993]. Administered intraperitoneally, caprolactam at doses of 350 to 600 mg/kg caused tremor, convulsions, and a bloody eye discharge [Hathaway et al. 1991]. Guinea pigs tolerated seven daily 7-hr exposures to a concentration of caprolactam ranging from 118 to 261 mg/m^3 without evidence of adverse effects, other than occasional coughing [ACGIH 1991]. A 2-year carcinogenicity study of caprolactam in rats and mice showed negative results [IARC 1986].

2. *Effects on Humans:* Caprolactam is a convulsant and an irritant of the eyes, nose, and throat in humans [ACGIH 1991]. Exposure to this substance has also caused skin sensitization in some individuals [ACGIH 1991]. Repeated contact of the skin with the solid causes only transient irritation, in contrast to prolonged contact with the dust, which causes dermatitis [ACGIH 1991]. At vapor concentrations that occasionally peaked at 100 ppm (460 mg/m^3), polymer plant workers reported experiencing severe and dose-related eye, nose, and throat irritation; eye irritation was not experienced below a concentration of 25 ppm, but transient nose and throat irritation occurred in some workers even at vapor concentrations of 10 ppm (46 mg/m^3) [ACGIH 1991]. Volunteers exposed to caprolactam vapor for unspecified periods at concentrations ranging from 53 to 521 mg/m^3 reported eye and upper respiratory tract irritation [ACGIH 1991]. A group of male workers exposed to caprolactam and other chemicals showed an increase in sperm abnormalities, and women occupationally exposed to this substance are reported to have experienced an increased rate of complications during pregnancy; however, confounding exposures and other methodological problems make interpretation of these results difficult [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to caprolactam vapor may cause redness, inflammation, and burning of the eyes; runny nose; scratchy throat; productive cough; transient skin redness; nose bleeds; a bitter taste in the mouth; and a feeling of nervousness.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to caprolactam vapor have been reported.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during an emergency.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve caprolactam vapor and may result in worker exposures to this substance:

—Use as a chemical intermediate in the production of nylon-6 fibers and plastics

—Use as a solvent for some high molecular weight polymers

—Use in making coatings, plasticizers, paint vehicles, and synthetic leather

The following methods are effective in controlling worker exposures to caprolactam vapor, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to caprolactam vapor, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to caprolactam vapor at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to caprolactam vapor exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of caprolactam vapor on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for caprolactam vapor.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne caprolactam vapor is determined by using an OSHA Versatile Sampler (OVS7), 13-mm XAD-7 tube (270/140-mg sections, 20/60 mesh), with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 100 liters (TWA) or 15 liters (STEL) is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If caprolactam vapor contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with caprolactam vapor should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laudering contaminated clothing should be informed of the hazardous properties of caprolactam vapor.

A worker who is exposed to caprolactam vapor should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where caprolactam vapor is present.

STORAGE

Caprolactam should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical equipment in use in storage areas should be of explosionproof design. Containers of caprolactam vapor should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained caprolactam vapor may still hold product residues, they should be handled appropriately.

LEAKS

In the event of a leak involving caprolactam vapor, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Do not touch the leaked material.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Cover the leaked material with sand, vermiculite, or soda ash and place material into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Caprolactam vapor is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of caprolactam vapor; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of caprolactam vapor emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although caprolactam vapor is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of caprolactam vapor exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with caprolactam vapor. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to caprolactam vapor permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to caprolactam vapor.

Safety glasses, goggles, or face shields should be worn during operations in which caprolactam vapor might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with caprolactam vapor. Contact lenses should not be worn if the potential exists for caprolactam vapor exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPTAFOL

INTRODUCTION

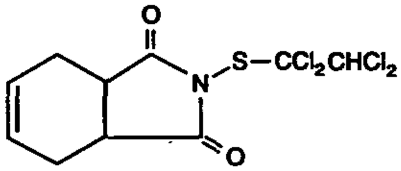
This guideline summarizes pertinent information about captafol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_9Cl_4NO_2S$

- **Structure**



- **Synonyms**

Difolatan; Captofol; Sanspor; Sulfonimide; 3a,4,7,7a-tetrahydro-2-((1,1,2,2-tetrachloroethyl)thio)-1-H-isoindole-1,3(2H)-dione; Alfloc 7020; Difosan; Folcid; Haipen 50; N-((1,1,2,2-tetrachloroethyl)sulfenyl)-cis-4-cyclohexene-1,2-dicarboximide; Nalco 7046; Ortho 5865; Proxel EF; cis-N-((1,1,2,2-tetrachloroethyl)thio)-4-cyclo-hexene-1,2-dicarboximide

- **Identifiers**

1. CAS No.: 2425-06-1
2. RTECS No.: GW4900000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Captafol is a noncombustible, white, crystalline substance with a characteristic odor. It is available commercially in the form of a liquid or wettable powder.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 349.06
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): Data not available
4. Vapor density: Not applicable
5. Melting point: 160° to 161°C (320° to 321.8°F) (decomposes)
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water; slightly soluble in acetone and most organic solvents; freely soluble in toluene.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Strongly alkaline conditions
2. Incompatibilities: Contact of captafol with acids or acid vapors may cause violent reactions.
3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen and sulfur) may be released in a fire involving captafol.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to captafol; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving captafol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving captafol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for captafol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure. However, captafol has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned captafol a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the sensitization effects associated with exposure to captafol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to captafol can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Captafol is a liver and kidney toxicant; it also has fetotoxic and teratogenic effects in experimental animals. When instilled into rabbits' eyes it caused irritation of the conjunctiva and iris that lasted 21 days [ACGIH 1991]. Moderate skin irritation resulted when rabbits were dermally exposed to captafol for 72 hr [ACGIH 1991]. The dermal LD_{50} in the rabbit is 9 g/kg while it is <15 g/kg for the 80% wettable powder [NLM 1991; ACGIH 1991]. Rat oral LD_{50}s range from 2.5 to 6.8 g/kg [ACGIH 1991]. Dogs given 100 or 300 mg/kg captafol (route not specified) in a 2-yr study developed mild anemia and showed growth deficiency; the livers and kidneys of these animals and those given 30 mg/kg were slightly enlarged but showed no functional abnormalities [Hayes 1982]. Captafol is fetotoxic and/or teratogenic in rats, rabbits, and hamsters by the oral or peritoneal routes of exposure [NIOSH 1991; NLM 1991]. Captafol is also an experimental mutagen: it was positive in one in vivo and several in vitro tests [NLM 1991]. In a 2-yr cancer bioassay, rats were fed captafol at dietary levels of 250, 500,

1,500, or 5,000 ppm. Animals in the two highest dose groups did not grow normally and had enlarged livers; mortality was increased in animals dosed at the highest level. On microscopic examination, the livers and kidneys of animals given 1,500 or 5,000 ppm captafol showed kidney and pronounced degenerative liver changes, although there was no evidence of tumors [Hayes 1982; Clayton and Clayton 1981]. A second chronic study has confirmed captafol to be a carcinogen in treated mice [ACGIH 1991].

2. *Effects on Humans:* In humans, captafol is an irritant and sensitizer of the skin and upper respiratory system. Reactions to acute overexposure to captafol may be severe; sensitized workers develop wheezing and bronchitis [Clayton and Clayton 1981]. A 1969 survey of Japanese farmers reported a 25% incidence of occupational dermatitis in these workers; those farmers who had developed acute contact dermatitis had been engaged in the application of captafol and had developed red and swollen eyelids and dermatitis that was aggravated by light (phototoxic dermatitis). The skin eruptions typically appeared 1 to 3 days after contact and usually disappeared within a week after the cessation of exposure [Hayes 1982]. In one study, 23% of agricultural workers exposed to captafol reported episodes that suggested occupationally induced dermatitis [NLM 1991]. Another study reports that many of the captafol-exposed workers who had developed skin rash also showed signs of systemic toxicity: hypertension, anemia, decreased liver function, decreased excretion of urinary protein and urobilinogen, and depressed cholinesterase activity [Hayes 1982; ACGIH 1991]. Ingestion of large quantities have caused vomiting and diarrhea [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Captafol can induce wheezing, bronchitis, coughing, redness and tearing of the eyes, red and swollen eyelids, and reddened and blistered skin.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to captafol may include raised, itching, reddened, and blistered eruptions of the skin, asthmatic wheezing, hypertension, anemia, and decreased red blood cell cholinesterase activity and elevated liver function.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if captafol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** use syrup of ipecac if large amounts of captafol are ingested.

—Do ***not*** induce vomiting if captafol has been mixed with a petroleum distillate such as kerosene or diesel fuel.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve captafol and may result in worker exposures to this substance:

—Manufacture of captafol or captafol mixtures

—Formulation of captafol-containing fungicides

—Application of captafol-containing fungicides to tomatoes, potatoes, coffee plants, logs, and wood products

The following methods are effective in controlling worker exposures to captafol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to captafol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to captafol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to captafol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of captafol on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for captafol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne captafol is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm tube (270/140 mg sections, 20/60 mesh) that has a glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 240 liters is collected. Analysis is conducted by gas chromatography using an electron capture detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989]

PERSONAL HYGIENE

If captafol contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with captafol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of captafol, particularly its potential to cause skin sensitization.

A worker who handles captafol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where captafol or a solution containing captafol is handled, processed, or stored.

STORAGE

Captafol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of captafol should be protected from physical damage and should be stored separately from acids, acid fumes, strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained captafol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving captafol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small dry spills, collect material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in an approved facility.

6. If captafol is in liquid or slurry form, absorb it with vermiculite, dry sand, earth, or a similar method.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Captafol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of captafol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of captafol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although captafol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of captafol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with captafol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to captafol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to captafol.

If captafol is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which captafol might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with captafol.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPTAN

INTRODUCTION

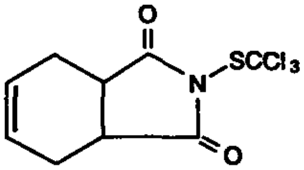
This guideline summarizes pertinent information about captan for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_9H_8Cl_3NO_2S$

- **Structure**



- **Synonyms**

  N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide; 3a,4,7,7a-tetrahydro-2-[(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione; AA Captan; Agrosol S; Agrox 2-Way and 3-Way; Amercide; Bangton; Bean Seed Protectant; Captaf; Captex; Esso Fungicide 406; Flit 406; Glyodex 37-22; Hexacap; Isotox Seed Treater "D" and "F"; Kaptan; Malipur; Merpan; Neracid; Orthocide; Vancide P-75; Vanicide

- **Identifiers**

  1. CAS No.: 133-06-2
  2. RTECS No.: GW5075000
  3. DOT UN: 9099 31
  4. DOT label: None

- **Appearance and odor**

  Captan is an odorless, white, crystalline solid that can also be found as a yellow powder. This substance is available as a powder or in a variety of liquid formulations.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 300.57
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity (water = 1): 1.74 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 178°C (352.4°F) (decomposes)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 25°C (77°F): Less than 0.00001 mm Hg

7. Solubility: Practically insoluble in water; soluble in acetone, benzene, chloroform, cyclohexanone, isopropanol, and xylene; insoluble in petroleum oils.

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and alkalinity

2. Incompatibilities: Tetraethyl pyrophosphate and emulsifiable concentrate formulations of parathion

3. Hazardous decomposition products: Toxic gases (such as chlorine, phosgene, and oxides of nitrogen and sulfur) may be released in a fire involving captan.

4. Special precautions: Captan cannot be used with strong alkalies or with oil sprays.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to captan; this substance may burn, but it does not ignite readily.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol foam.

Fires involving captan should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of captan may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving captan. Structural firefighters' protective clothing may provide limited protection against fires involving captan.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for captan [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. However, captan has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned captan a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer that is associated with exposure to captan [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to captan can occur through inhalation, ingestion, and eye and skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, captan is an irritant and sensitizer of the skin. When applied to the skin of experimental animals (species not identified) at a dose of 900 mg/kg, captan caused slight irritation [ACGIH 1991], while previously exposed guinea pigs developed a moderate degree of sensitization when rechallenged [Clayton and Clayton 1981]. The dermal LD$_{50}$ in rabbits is greater than 9 g/kg [Clayton and Clayton 1981]. The 2-hr LC$_{50}$s for male and female mice are 4,500 and 5,000 mg captan/m^3, respectively [ACGIH 1991]. However, mechanical

milling of that technical material reduced the 2-hr LC_{50}s in mice to 1,700 and 3,700 mg/m^3, respectively. Estimated inhalation absorption levels for the milled material were calculated to be 142 mg/kg for the males and 310 mg/kg for the females. The 2-hr LC_{50} for rats is greater than 5,700 mg/m^3 for unmilled captan [Stevens et al. 1978]. The lowest reported oral LD50s in mice and rats are 7,500 and 8,400 mg/kg [ACGIH 1991; IARC 1983]. Laboratory animals given very high doses (not further specified) of captan became hypothermic, irritable, anorectic, and listless; they also had hyporeflexia and oliguria [EPA 1989]. When tested in mice, rats, dogs, and monkeys at doses below those that are maternally toxic, captan failed to produce teratogenic effects by the oral, subcutaneous, or inhalation route of administration [Hayes 1982]. Although captan has not been shown to be teratogenic, feeding at maternally toxic doses has caused fetotoxicity (increased resorptions and decreased fetal weights) and possible terata (e.g., shortened forelimbs, cleft palate, fused ribs, exencephaly) among the offspring of some species [NLM 1991; IARC 1983]. Feeding studies demonstrated no effects in dogs fed 100 mg/kg/day for 66 weeks, but feeding at a dose of 300 mg/kg/day caused a slight increase in liver and kidney weights [Hayes 1982; ACGIH 1991]. Female rats fed 1,000 or 5,000 ppm captan in their diet (about 250 mg/kg/day) for 2 yr showed growth retardation; at twice this dose, captan caused growth depression in animals of both sexes and testicular atrophy in the males [Clayton and Clayton 1981; Hayes 1982]. Captan is mutagenic in direct contact with susceptible cells, but it is not mutagenic in intact animals, except perhaps at very high doses [Hayes 1982]. Captan was tested for carcinogenicity in mice and rats by dietary administration; it was carcinogenic in one strain of mice, in which it caused a statistically significant increase in the incidence of duodenal tumors [IARC 1983]. The International Agency for Research on Cancer (IARC) has concluded that there is limited evidence that captan is carcinogenic in experimental animals [IARC 1983]. Subsequent to the IARC review, rats and mice that were administered captan in their diets for 80 weeks developed neoplasms, including cancers. Rats developed neoplasms of the ovary, liver, and the pituitary, adrenal, and mammary glands. Mice had increased numbers of duodenal neoplasms [NLM 1991].

2. *Effects on Humans:* In humans, captan is an irritant of the eyes, skin, and upper respiratory tract and a skin sensitizer [Hayes 1982; Klaassen et al. 1986; Clayton and Clayton 1981]. Skin contact with captan has caused severe sensitivity in some workers, and an estimated 3% to 5% of the exposed population could become sensitized [IARC 1983]. An 18-year-old gardener was confirmed as having recurrent urticaria from exposure to captan [NLM 1991]. A 1,071 mg/kg dose of captan caused the death of one individual [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Captan can induce redness, pain, and tearing of the eyes; runny nose; scratchy throat; difficult breathing; and redness, itching, and cracking of the skin.

2. *Chronic exposure:* Captan-sensitized workers can develop redness, raised areas, blistering, and itching of the skin.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if captan or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve captan and may result in worker exposures to this substance:

—Manufacture and formulation of captan-containing fungicides and bactericides

—Use as a fungicide to control scab, black root, botrytis, sooty blotch, and summer rots on apples and for control of a wide variety of fungal diseases on small fruits, berries, vegetables, and ornamental crops

—Use as a bacteriostat in soaps

—Use as a fungicide in paints, lacquers, paper, rubber stabilizers, vinyl resins, plastics, leather fabrics, and to preserve cosmetics and fruits

—Use as a bacteriostat and fungicide in veterinary medicine

The following methods are effective in controlling worker exposures to captan, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to captan, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to captan at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory tract or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to captan exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of captan on the respiratory tract or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for captan.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne captan is determined by using an OSHA Versatile Sample (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If captan contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with captan should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of captan, particularly its potential to cause skin sensitization.

A worker who handles captan should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where captan or a solution containing captan is handled, processed, or stored.

STORAGE

Captan should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of captan should be protected from physical damage and should be stored separately from water and heat. Because containers that formerly contained captan may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving captan, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the captan for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Captan is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for captan is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of captan per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of captan emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although captan is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of captan exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with captan. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to captan permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to captan.

If captan is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which captan might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with captan. Contact lenses should not be worn if the potential exists for captan exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBARYL

INTRODUCTION

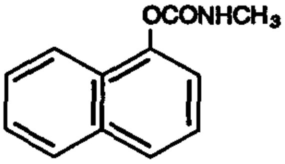
This guideline summarizes pertinent information about carbaryl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{11}NO_2$

- **Structure**



- **Synonyms**

Sevin, 1-naphthyl n-methylcarbamate, alpha-naphthyl n-methylcarbamate, methylcarbamic acid-1-naphthyl ester

- **Identifiers**

1. CAS No.: 63-25-2
2. RTECS No.: FC5950000
3. DOT UN: 2757 55
4. DOT label: None

- **Appearance and odor**

Carbaryl is an odorless white, gray, or colorless solid. This substance is a carbamate pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 201.22
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.23 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 142°C (287.6°F)
6. Vapor pressure at 25°C (77°F): <0.00004 mm Hg
7. Solubility: Nearly insoluble in water; moderately soluble in dimethylformamide, acetone, isophorone, and cyclohexanone.
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Unstable above 70°C (148°F); hydrolyzes in alkalies

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2. Incompatibilities: Contact of carbaryl with strong oxidizers may cause fires and explosions. Carbaryl is also incompatible with strongly alkaline pesticides.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, methylamine, and carbon monoxide) may be released in a fire involving carbaryl.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to carbaryl. This substance is not flammable, although other constituents of carbaryl formulations may be flammable or combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinquishant that is suitable for the materials involved in the surrounding fire.

Fires involving carbaryl should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbaryl formulations may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbaryl. Chemical protective clothing that is specifically recommended for carbaryl may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving carbaryl.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbaryl is 5 mg/m^3 as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for carbaryl is 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbaryl a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of teratogenic, systemic, and other effects associated with exposure to carbaryl, and the NIOSH limit is based on the risk of central nervous system and reproductive effects associated with exposure to carbaryl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbaryl can occur through inhalation, eye and skin contact, percutaneous absorption, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Carbaryl inhibits cholinesterase enzyme activity in the central, autonomic, and peripheral nervous systems. This chemical was mildly irritating to exposed rabbit eyes and severely irritating to rabbit skin following a 24-hr contact period [NIOSH 1992b]. Guinea pigs showed a weak skin sensitization reaction to carbaryl [Carpenter et al. 1961]. The dermal LD_{50} is 4,000 mg/kg for rats and 2,000 mg/kg for rabbits [NIOSH 1992b]. Goats acutely drenched with carbaryl developed anorexia, diarrhea, dullness, weakness, frothing, nasal discharge, recumbency, and death. Histopathology of necropsied tissues revealed hyperemia of the CNS, heart, liver, and kidney plus myocardial and neuronal degeneration [NLM 1992]. The lowest reported oral LD_{50} for mice is 128 mg/kg, and for rats it is 230 mg/kg [NIOSH 1992b]. Dogs were given a single

oral dose of carbaryl (250, 375, or 500 mg/kg); animals in the two higher dose groups showed signs of nervous system stimulation: lacrimation, excessive salivation, muscular twitching, incoordination, vomiting, defecation, and urination [Carpenter et al. 1961]. In the dogs given 375 mg/kg carbaryl, red blood cell cholinesterase activity was depressed by 24% to 33% [Carpenter et al. 1961]. Rats that received doses ranging from 7 to 70 mg/kg for up to 12 months developed marked functional and structural changes of the pituitary gland plus impairment of thyroid and gonadal function [IARC 1976]. Long-term exposure of pigs resulted in the induction of a progressive structural neuromyopathy that was not acutely reversible with atropine [NIOSH 1992b]. Male rats exposed to 200 mg/kg three times a week for 13 weeks did not develop adverse reproductive effects, but doses of 70 mg/kg (dosing schedule undefined) for 1 year caused reduced sperm motility and alterations in spermatogenesis [NIOSH 1992b]. Female rats exposed to a total dose of 1,370 mg/kg over 39 weeks developed menstrual cycle changes, and exposure of other rats to 5,475 mg/kg over 52 weeks caused uterine, cervix, vaginal, ovarian, and fallopian tube alterations [NIOSH 1992b]. Carbaryl has not been shown to be teratogenic at doses below those causing maternal toxicity [Proctor et al. 1988]. Carbaryl is a mutagen in a wide variety of in vitro and in vivo tests [NIOSH 1992b]. Based on a review of the results of carcinogenicity bioassays in mice and rats, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of this substance in animals is inadequate [IARC 1987].

2. *Effects on Humans:* Carbaryl causes reversible cholinesterase inhibition in humans; this effect causes acetylcholine to accumulate at synapses in the nervous system, at neuromuscular junctions of the skeletal and smooth muscles, and in the secretory glands. In two separate incidents, a liquid insecticide (carbaryl/dimethoate mixture) was splashed into a person's eyes, causing transient injury to the corneal epithelium and swelling of the lids [NIOSH 1992b]. Dermal application of carbaryl to the forearm resulted in urinary excretion of 74% of the dose applied [IARC 1976]. A single oral dose of 250 mg carbaryl (approximately 2.8 mg/kg) caused the sudden onset of abdominal pain followed by profuse sweating, lethargy, and vomiting in an adult man; after treatment, this individual recovered completely. An individual who had consumed 21 g of carbaryl (500 mg/kg) recovered from acute cholinesterase inhibition but suffered weakness of the arms and legs and had electrophysiologic findings consistent with a diagnosis of peripheral neuropathy [NIOSH 1992b]. A 75-year-old man who had excessive long-term exposure to carbaryl recovered from cholinesterase inhibition when removed from exposure, but sleep apnea and peripheral neuropathy appeared as late clinical features [NIOSH 1992b]. A group of 59 workers exposed for 19 months to carbaryl concentrations ranging from 0.23 to 31 mg/m^3 showed no overt signs or symptoms of carbamate poisoning, although their red blood cell cholinesterase activity was slightly depressed [Proctor et al. 1988]. Testicular dysfunction and abnormalities in the shape of sperm have been reported in carbaryl-exposed workers [Schrag and Dixon 1985; Wyrobek et al. 1980, 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbaryl-induced chloinesterase inhibition can cause nausea, vomiting, abdominal cramps, and diarrhea; excessive sweating and salivation; lethargy and weakness; runny nose and a sensation of tightness in the chest; contracted pupils, blurred vision, tearing, and pain in the eyes; loss of coordination, tremors, and slurring of speech; increasingly difficult respiration, convulsions, and coma. If the poisoning is severe, death from respiratory failure may follow.

2. *Chronic exposure:* Carbaryl has induced headache, memory loss, anorexia, weight loss, proximal muscle weakness, fasciculations, cramps, sleep apnea, and peripheral neuropathy.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbaryl or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** induce vomiting if carbaryl has been mixed with a petroleum distillate such as kerosene or diesel fuel.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The use of carbaryl as a molluscicide, acaricide, and insecticide (for fruits, vegetables, cotton, tobacco, ornamental trees, livestock, poultry, and pets) may result in worker exposure to this chemical.

The following methods are effective in controlling worker exposures to carbaryl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbaryl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the red blood cell cholinesterase activity.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbaryl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with cholinesterase inhibition.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbaryl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbaryl on red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. A pre-exposure blood cholinesterase concentration should be obtained for each worker so that the postexposure concentration may be expressed as a percentage of that subject's normal cholinesterase activity. A postexposure blood cholinesterase concentration that is less than 70% of normal is considered indicative of excessive exposure to carbaryl. Although the relationship between airborne concentrations of carbaryl and urinary concentrations of 1-naphthal has not been established, urinary concentrations of 1-naphthal in excess of 4 mg/liter urine may reflect overexposure to carbaryl.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbaryl is determined by an OSHA versatile sampler (OVS-2) containing two sections of XAD-2 resin (270/140-mg sections, 20/60 mesh) and a glass fiber filter. Sampling tubes can be obtained from OSHA's Salt Lake City Analytical Laboratory. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 60 liters is collected. The samples are extracted with acetonitrile. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is 0.08 mg/m^3. This method is described in Method No. 63, OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If carbaryl contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with carbaryl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbaryl, particularly its potential to cause cholinesterase inhibition.

A worker who handles carbaryl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbaryl or a solution containing carbaryl is handled, processed, or stored.

STORAGE

Carbaryl should be stored in a cool, dry, continuously ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbaryl should be protected from physical damage and should be stored separately from strong oxidizers, strongly alkaline pesticides, heat, sparks, and open flame. Because containers that formerly contained carbaryl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbaryl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the carbaryl for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbaryl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbaryl is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of carbaryl per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbaryl emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbaryl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbaryl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, full-body coveralls, and impervious footwear) should be worn to prevent repeated or prolonged skin contact with carbaryl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by carbaryl and may provide protection for more than 4 but fewer than 8 hr: natural rubber, neoprene, nitrile rubber, and polyvinyl chloride.

If carbaryl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbaryl might contact the eyes (e.g., through splashes of carbaryl-containing formulations). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbaryl. Contact lenses should not be worn if the potential exists for carbaryl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBOFURAN

INTRODUCTION

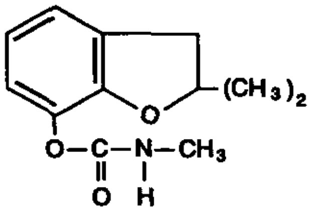
This guideline summarizes pertinent information about carbofuran for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{15}NO_3$

- **Structure**



- **Synonyms**

Bay 70143; Niagra 10242; Furadan; Furodan; Yaltox; Curaterr; Chinufur; 2,2-dimethyl-2,2-dihydrobenzofuranyl-7-N-methylcarbamate; methyl carbamic acid 2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester

- **Identifiers**

1. CAS No.: 1563-66-2
2. RTECS No.: FB9450000
3. DOT UN: 2757 55
4. DOT label: Poison B

- **Appearance and odor**

Carbofuran is a noncombustible, odorless, colorless or white crystalline solid available commercially in the form of wettable powder, granules, or flowable paste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 221.26
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.18 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of carbofuran): Data not available
5. Melting point: 150° to 152°C (302° to 305.6°F)
6. Vapor pressure at 33°C (91.4°F): 0.00002 mm Hg
7. Solubility: Slightly soluble in water; soluble in ace-

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tone, acetonitrile, benzene, cyclohexanone, and other organic solvents. In the conventional solvent formulations used in agriculture, carbofuran is essentially insoluble.

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, flame, or contact with an alkaline substance

2. Incompatibilities: Fires and explosions may result from contact of carbofuran with alkaline media, acids, or strong oxidizers (such as perchlorates, peroxides, chlorates, nitrates, and permanganates).

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving carbofuran.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to carbofuran; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving carbofuran.

Fires involving carbofuran should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbofuran may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbofuran. Chemical protective clothing that is specifically recommended for carbofuran may provide little or no thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving carbofuran.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for carbofuran [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbofuran a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to carbofuran.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbofuran can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbofuran is a potent but reversible cholinesterase inhibitor. Instillation of carbofuran into the conjunctival sac caused miosis and paralysis of the ciliary muscle, both reversed by installation of atropine [Tobin 1970]. There are widely divergent dermal LD$_{50}$s for rabbits which range from 885 mg/kg [NIOSH 1992b] to 10,200 mg (98% carbofuran)/kg [Tobin 1970]. The rat dermal LD$_{50}$ is 120 mg/kg [NIOSH 1992b]. The LC$_{50}$ in rats is 85

mg/m^3 for an unspecified period [NIOSH 1992b]. Monkeys which inhaled a 75% wettable powder (wp) dust for 6 hr at an airborne concentration of 0.86 mg/m^3 showed slight but significant cholinesterase inhibition; at an exposure of 0.56 mg/m^3 for the same period, no effects were seen. In addition, a monkey had sporadic tremors following a 30-min exposure to 1.3 mg/m^3. Another exposed to 1.8 mg/m^3 for 260 min developed only emesis [Tobin 1970]. The oral LD$_{50}$s for mice, rats, and dogs are 2, 5, and 19 mg/kg, respectively [NIOSH 1992b]. In experimental animals given high but non-lethal doses of carbofuran, normal cholinesterase activity returned within 6 hr [NLM 1991]. Dogs fed 50 ppm carbofuran in a chronic feeding study (length of study not specified) showed significant inhibition of plasma, erythrocyte, and brain cholinesterase levels; the no-effect levels in dogs and rats were 20 ppm (dogs) and 25 ppm (rats) [ACGIH 1991]. Administered to rats by gavage on day 18 of gestation, a dose of 2.5 mg/kg carbofuran produced cholinergic signs within 5 minutes and killed 25% of the dams within 30 minutes; a dose of 0.05 mg/kg produced nervous system effects in the dams but not in the fetuses [Hayes 1982]. No adverse reproductive or developmental effects were induced in three successive generations of rats which consumed diet containing carbofuran (10 mg/kg diet) or in dogs on a 50 mg carbofuran/kg diet for one generation [NIOSH 1992b]. When mice, rats, rabbits, and dogs consumed diets containing carbofuran (100 mg/kg), the only effect induced was decreased survival rates in rat pups [Shepard 1986]. Carbofuran is mutagenic in bacterial and mammalian test systems [NIOSH 1992b; NLM 1991].

2. *Effects on Humans:* In humans, carbofuran is a rapidly reversible cholinesterase inhibitor. No effects have been reported in workers exposed to carbofuran concentrations approaching 0.1 mg/m^3 per day [NLM 1991]. Several cases of carbofuran poisoning have been reported in laboratory and pilot plant personnel and applicators. These workers developed weakness, malaise, profuse perspiration, lightheadedness, paleness, nausea, blurred vision, loss of depth perception, hypersalivation, poor coordination, and vomiting. Recovery took up to 4 hr in the absence of atropine treatment and less than 30 min when it was administered. No systemic toxicity was observed when only ocular effects were induced [Tobin 1970]. Seventy-four of 142 teenage workers who worked in a field that had been sprayed with carbofuran the previous day experienced pronounced symptoms of nervous system poisoning, including dizziness, nausea, and/or blurred vision; however, all of these workers responded quickly and completely to therapy [Hayes 1982]. Carbofuran is mutagenic in human lymphocyte cells [NIOSH 1992b].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbofuran can cause muscle weakness, dizziness, profuse sweating, headache, salivation, nausea, vomiting, abdominal pain, diarrhea, contracted pupils, incoordination, slurred speech, difficult breathing, chest tightness, blurred vision, muscle twitching and spasms. Convulsions may occur.

2. *Chronic exposure:* Based on effects seen in animals, long-term exposure to low levels of carbofuran is likely to cause cholinesterase inhibition.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure: **Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Carbofuran can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbofuran or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** induce vomiting if carbofuran has been mixed with a petroleum distillate such as kerosene or diesel fuel.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbofuran and may result in worker exposures to this substance:

—Use as an acaricide, miticide, nematocide, and insecticide

—Manufacture of carbofuran

—Formulation of carbofuran for use as a pesticide

The following methods are effective in controlling worker exposures to carbofuran, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbofuran, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood and on the individual's pre-exposure plasma and red blood cell cholinesterase activity levels.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbofuran at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma or red blood cell cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbofuran exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbofuran on plasma or red blood cell cholinesterase activity levels. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of overexposure to organophosphorus compounds such as carbofuran. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for carbofuran (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability. Absorption of carbofuran can be confirmed by analysis of urine for its metabolite, carbofuran phenol. However, correlations between airborne and urinary levels of carbofuran and its metabolite have not been established.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbofuran is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/60 mesh). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 480 liters is collected. The sample is then treated with acetonitrile to extract the carbofuran. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If carbofuran contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with carbofuran should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbofuran.

A worker who handles carbofuran should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbofuran or a solution containing carbofuran is handled, processed, or stored.

STORAGE

Carbofuran should be stored in a cool, dry, continuously-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbofuran should be protected from physical damage and should be stored separately from acids, strong oxidizers (such as perchlorates, peroxides, and nitrates), heat, sparks, and open flame. Because containers that formerly contained carbofuran may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbofuran, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.
5. For liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility at which there are 10,000 lb or more of carbofuran must comply with EPA's emergency planning requirements. (If carbofuran is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of carbofuran are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for carbofuran is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbofuran emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbofuran is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbofuran exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with carbofuran. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to carbofuran permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to carbofuran.

If carbofuran is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbofuran might contact the eyes (e.g., through dust particles or splashes of carbofuran-containing solutions). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbofuran. Contact lenses should not be worn if the potential exists for carbofuran exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
CARBON BLACK
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about carbon black and carbon black containing polycyclic aromatic hydrocarbons (PAH's) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Synonyms:** Channel black, furnace black, thermal black
- **Identifiers:** CAS 1333-86-4; RTECS FF5800000; DOT Not assigned
- **Appearance and odor:** Odorless black solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Specific gravity (water = 1): 1.8 to 2.18
2. Vapor pressure at 20°C (68°F): Essentially zero
3. Insoluble in water

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers (e.g., chlorates, bromates, and nitrates) may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving carbon black.
3. Caution: Carbon black dust may form explosive mixtures in air.

- **Flammability**

1. Minimum dust ignition temperature: 510°C (950°F)
2. Extinguishant: Water or carbon dioxide
3. Combustible solid, (NFPA)

- **Warning properties**

1. Evaluation of warning properties for respirator selection (carbon black): Based on lack of information on irritation levels, carbon black should be considered to have poor warning properties.
2. Evaluation of warning properties for respirator selection (carbon black containing PAH's): Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbon black is 3.5 milligrams of carbon black per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for carbon black is 3.5 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. NIOSH recommends that carbon black containing PAH's at a concentration greater than 0.1% be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH REL for PAH's that may be formed during the manufacture of carbon black and that could be adsorbed on the carbon black is 0.1 mg/m^3 (measured as the cyclohexane-extractable fraction) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 3.5 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for carbon black

	Exposure limits mg/m^3
OSHA PEL TWA	3.5
NIOSH REL TWA (carbon black)	3.5
TWA (PAH's) (Ca)*	0.1
ACGIH TLV® TWA	3.5

* (Ca): NIOSH recommends treating as a potential human carcinogen when the concentration of PAH's is greater than 0.1%.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon black may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Summary of toxicology**

1. *Effects on animals:* Inhalation of carbon black by mice, rats, and monkeys caused thickened alveolar walls, increased pulmonary collagen, right atrial and ventricular strain, hypertrophy of the right and left ventricles and septum, and increased heart weights. Although carbon black itself did not cause cancer in treated animals, carbon black containing polynuclear hydrocarbons (PNA's) or PAH's did cause cancer following chronic administration by all routes tested.
2. *Effects on humans:* Chronic inhalation exposure of production workers has caused decreased pulmonary function and myocardial dystrophy. There is suggestive but inconclusive evidence that carbon black containing PAH's has been responsible for induction of skin cancer in exposed workers.

- **Signs and symptoms of exposure**

Long-term (chronic): Inhalation of carbon black can cause cough, phlegm, tiredness, chest pain, and headache. Dermal, mucosal, or inhalation exposure can cause irritation.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to carbon black, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to carbon black at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to carbon black. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to carbon black may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to carbon black should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting carbon black particulate with tared 5 μm PVC membrane filters and analyzing by gravimetric methods. A detailed sampling and analytical method for carbon black may be found in the *NIOSH Manual of Analytical Methods* (method number 5000). Sampling and analysis of PAH's present in the particulate or the filters may be performed by extracting with cyclohexane (aided by sonification), filtering through a fritted glass funnel, and weighing a dried aliquot of the extract. A detailed sampling and analytical method for cyclohexane-extractable PAH's may be found in *Criteria for a Recommended Standard. . . .Occupational Exposure to Carbon Black.*

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with carbon black.

Workers should be provided with and required to use dust-proof safety goggles where carbon black may come in contact with the eyes.

SANITATION

Clothing which is contaminated with carbon black should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon black from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of carbon black's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with carbon black should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle carbon black should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to carbon black may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for carbon black

Operations	Controls
During the manufacture of natural and synthetic rubber, dry cells, explosives, plastics, and paper	Local exhaust ventilation, personal protective equipment
During the manufacture and distribution of carbon black; during maintenance of equipment and storage containers	Local exhaust ventilation, personal protective equipment
During the manufacture and use of coatings and printing inks; during use as a coloring pigment and source of carbon	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to carbon black, an eye-wash fountain should be provided within the immediate work area for emergency use.

If carbon black gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to carbon black containing PAH's, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If carbon black gets on the skin, wash it immediately with soap and water. If carbon black penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If carbon black is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Carbon black dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it should then be placed in an appropriate container. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Tables 3 and 4).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed in Table 3. All respirators that have higher protection factors may also be used. Table 4 lists respirators for protection against carcinogens, which includes only those respirators providing the highest protection factor available.

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Table 3.—Respiratory protection for carbon black

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 17.5 mg/m³	Any dust and mist respirator
Less than or equal to 35 mg/m³	Any dust and mist respirator except single-use and quarter-mask respirators
	Any supplied-air respirator
	Any air-purifying respirator with a high-efficiency particulate filter
	Any self-contained breathing apparatus
Less than or equal to 87.5 mg/m³	Any powered air-purifying respirator with a dust and mist filter
	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 175 mg/m³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 3,500 mg/m³	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 3,500 mg/m³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 3.5 mg/m³ (TWA).

Table 4.—Respiratory protection for carbon black containing greater than 0.1% PAH's

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Carbon Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CO_2
- Synonyms: Carbonic acid gas; "Dry Ice"; CO_2
- Appearance and odor: Primarily a colorless, odorless gas; however, it can be a liquid or a solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon dioxide is 5000 parts of carbon dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9000 milligrams of carbon dioxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 10,000 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 30,000 ppm averaged over a 10-minute period. The NIOSH Criteria Document for Carbon Dioxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon dioxide can affect the body if it is inhaled. Solid carbon dioxide (dry ice) and compressed carbon dioxide gas from a cylinder can affect the body if it comes in contact with the eyes, skin, or mouth.

- **Effects of overexposure**

Inhaling carbon dioxide may cause rapid breathing, rapid beating of the heart, headache, sweating, shortness of breath, dizziness, mental depression, visual disturbances, shaking, unconsciousness, and death. Skin, eye, or mouth contact with solid carbon dioxide (dry ice) may cause frostbite. Similar effects may occur from carbon dioxide as it is being released from a cylinder.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon dioxide.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to carbon dioxide at potentially hazardous levels.

- **Summary of toxicology**

Carbon dioxide gas is an asphyxiant, a potent respiratory stimulant, and both a stimulant and depressant of the CNS. Respiratory volume is doubled at 4% CO_2 and redoubled at 5%. Increases in heart rate and blood pressure have been noted at 7.6% and dyspnea, headache, dizziness, and sweating occur if exposure at that level is prolonged. At 10% and above, prolonged exposure can result in unconsciousness. Above 11%, unconsciousness occurs in 1 minute or less. Numerous human fatalities have occurred after persons entered fermentation vats, wells, and silos where oxygen had been largely replaced by carbon dioxide. Exposure to very high concentrations, 25 to 30%, may cause convulsions. Carbon dioxide at room temperature will not injure the skin, but frostbite may result from contact with the solid or the liquid phases.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44
2. Boiling point (760 mm Hg): −78.5 C (−109 F) (sublimation point)
3. Specific gravity (water = 1): 1.02 (liquid)
4. Vapor density (air = 1 at boiling point of carbon dioxide): 1.52
5. Melting point: −78.5 C (-109 F) (sublimation point)
6. Vapor pressure at 20 C (68 F): Greater than 1

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atmosphere

7. Solubility in water, g/100 g water at 20 C (68 F): 0.14

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: Contact with chemically active metals such as sodium, potassium, or hot titanium may cause fire.

3. Hazardous decomposition products: None

4. Special precautions: Liquid or solid carbon dioxide will attack some forms of plastics, rubber, and coatings. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that carbon dioxide is an odorless gas.

2. Irritation Levels: Grant states that "carbon dioxide at high concentration in air causes a stinging sensation in the eyes, nose, and throat...."

3. Evaluation of Warning Properties: Since carbon dioxide has no odor, and since no quantitative information is available relating its irritant effects of to air concentrations, this gas has been treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon dioxide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of carbon dioxide in a gas sampling bag, followed by gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon dioxide may be used. An analytical method for carbon dioxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with solid carbon dioxide or from contact with vessels containing carbon dioxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fermentation in manholes, mine floors, wells, shipwells, brewery vats, garbage dumps, and fruit storage facilities	General dilution ventilation; local exhaust ventilation; personal protective equipment

Operation	Controls
Use in cooling and refrigerating for storage, preparation and transfer of foods; use as an inert gas in fire extinguishers; for protection of flammable materials during manufacture; in shielded arc welding; and in canned food production	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an inert pressure medium for aerosol packaging; pressure spraying, spray painting, gas-operated firearms, purging tanks and pipelines, inflating liferafts, manufacture of plastic foam	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of carbonated beverages	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a neutralizing agent in textile processing and treatment of leather hides; use as shattering agent for coal mining; in fracturing and acidizing treatment of oil and gas wells	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during water treatment for neutralizing alkaline waste waters; carbonating water to prevent scaling; use for chemical synthesis and pH control in manufacture of urea, asprin, carbonates and bicarbonates, beer, and sugar	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in miscellaneous operations for enrichment of greenhouse air, antiseptic, industrial solvent extraction, medical use, in foundries, cement curing, and in animal slaughter	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid carbon dioxide (dry ice) or carbon dioxide as it is being released from a cylinder gets into the eyes, get medical attention.

- **Skin or Mouth Exposure**

If solid carbon dioxide (dry ice) or carbon dioxide as it is being released from a cylinder comes in contact with the skin or mouth, stop the exposure immediately. If frostbite has occurred, get medical attention.

- **Breathing**

If a person breathes in large amounts of carbon dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If carbon dioxide is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR CARBON DIOXIDE

Condition	**Minimum Respiratory Protection* Required Above 5000 ppm**
Gas Concentration	
50,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Carbon Disulfide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CS_2
- Synonyms: Carbon bisulfide
- Appearance and odor: Colorless to faintly yellow liquid with a strong, disagreeable or sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon disulfide is 20 parts of carbon disulfide per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 30 ppm, and an acceptable peak of 100 ppm for 30 minutes in an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 10 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Carbon Disulfide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon disulfide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of carbon disulfide vapor may cause headache, nausea, drop in blood pressure, dizziness, unconsciousness, and death. Liquid carbon disulfide and high concentrations of the vapor may cause irritation of the skin, eyes, and nose. If the liquid is trapped under clothing, it may cause a burn. Swallowing carbon disulfide may cause loss of consciousness and convulsions. If small amounts are swallowed, vomiting, diarrhea, and headache may occur.

2. Long-term Exposure: Prolonged or repeated exposure to carbon disulfide may damage the nervous system and cause muscle weakness, numbness, feelings of pins and needles, unsteady walking, and difficulty in swallowing. Palsy, speech difficulty, and muscle spacticity may also occur. In addition, memory loss, headache, difficulty in sleeping, nervousness, fatigue, irritability, depression, suicidal tendencies, and psychosis may occur. Eye damage may occur with such symptoms as blind spots, narrowing of vision, and decreased ability to see in the dark. Increased arteriosclerosis may occur which may cause or increase damage to the heart and other organs. High blood pressure, kidney damage, liver damage, and stomach problems may occur. Repeated or prolonged exposure of the skin to carbon disulfide may cause a skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon disulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to carbon disulfide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems, eyes, cardiovascular system, kidneys, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to carbon disulfide, a urinalysis

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should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to carbon disulfide, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—An electrocardiogram: Carbon disulfide has caused arrhythmias and electrocardiographic changes in humans. Periodic surveillance is indicated.

—Ophthalmic examination: Carbon disulfide has caused ocular changes in humans. An ophthalmic examination should be performed, including visual acuity.

—Medical warning: Workers should be informed of potential undesirable effects of exposure to carbon disulfide on reproduction (such as spermatic deficiences, menstrual disorders, and spontaneous abortions).

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Carbon disulfide vapor causes narcosis at high concentrations; repeated exposure to low concentrations causes damage to the central and peripheral nervous systems and may accelerate the development of or worsen coronary heart disease. Exposure of humans to 1150 ppm causes serious symptoms, and 4800 ppm for 30 minutes may be fatal. Carbon disulfide intoxication can involve all parts of the central and peripheral nervous systems, including damage to the cranial nerves and development of polyneuritis with paresthesias and muscle weakness in the extremities, unsteady gait, and dysphagia. In extreme cases of intoxication, a Parkinson-like syndrome may result, characterized by speech disturbances, muscle spasticity, tremor, memory loss, mental depression, and marked psychic symptoms; permanent disability is likely. Reproductive disorders occur, such as aspermia, menstrual irregularities, and spontaneous abortion. Psychosis and suicide are established risks of overexposure to carbon disulfide. Other reported effects of exposure to carbon disulfide are ocular changes (retinal degeneration, corneal opacities, disturbances of color vision, corneal anesthesia, diminished pupillary reflexes, microscopic aneurysms in the retina), gastrointestinal disturbances (chronic gastritis and achlorhydria), renal impairment (albuminuria, microhematuria, elevated blood urea nitrogen, diastolic hypertension), and liver damage. Effects commonly caused by repeated exposure to carbon disulfide vapor are exemplified by a group of workers with a time-weighted average (TWA) exposure of 11.2 ppm (range 0.9 to 127 ppm) who complained of headaches and dizziness; in other workers with a TWA of 186 ppm (range 23 to 378 ppm) complaints also included sleep disturbances, fatigue, nervousness, anorexia, and weight loss; the end-of-day exposure coefficient of the iodine azide test on urine was a good indicator of workers who were or had been symptomatic. Overexposure to carbon disulfide has long been regarded as potentially atherogenic for cerebral, renal, and coronary arteries; recent epidemiologic studies of viscose rayon workers have confirmed a 2.5- to 5-fold increase in risk of death from coronary heart disease as compared with the experience of unexposed workers. Other cardiovascular effects observed in workers repeatedly exposed to carbon disulfide are bradycardia, tachycardia, arrhythmias, and electrocardiographic changes consistent with both nonspecific and ischemic wave changes. Splashes of the liquid in the eyes cause immediate and severe irritation; dermatitis and vesiculation may result from skin contact with the vapor or the liquid. Although ingestion is unlikely to occur, it may cause coma and convulsions.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76.1
2. Boiling point (760 mm Hg): 46.3 C (115 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of carbon disulfide): 2.6
5. Melting point: −111.5 C (-169 F)
6. Vapor pressure at 20 C (68 F): 300 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): 22.6

- **Reactivity**

1. Conditions contributing to instability: Containers may burst when heated.
2. Incompatibilities: Contact with strong oxidizers, and chemically active metals (such as sodium, potassium, and zinc), azides, and organic amines may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and carbon monoxide) may be released in a fire involving carbon disulfide.
4. Special precautions: Liquid carbon disulfide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −30 C (-22 F) (closed cup)
2. Autoignition temperature: 90 C (194 F)
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 50
4. Extinguishant: Dry chemical, carbon dioxide for small fires

- **Warning properties**

1. Odor Threshold: The *Handbook of Organic Industrial Solvents* states that at less than 1 ppm, carbon disulfide has a disagreeable odor. Summer gives an odor threshold of 7.7 ppm , and May gives 0.0011 ppm and 0.0081 ppm. The AIHA *Hygienic Guide* gives an odor threshold of 1.2 ppm.
2. Eye Irritation Level: Carbon disulfide is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of carbon disulfide is below the permissible

exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon disulfide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of carbon disulfide. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of carbon disulfide vapors using an adsorption tube with subsequent desorption with benzene and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon disulfide may be used. An analytical method for carbon disulfide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid carbon disulfide, where skin contact may occur.
- Non-impervious clothing which becomes contaminated with carbon disulfide should be removed promptly and not reworn until the carbon disulfide is removed from the clothing.
- Any clothing which becomes wet with liquid carbon disulfide should be removed immediately and not reworn until the carbon disulfide is removed from the clothing.
- Clothing wet with liquid carbon disulfide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon disulfide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the carbon disulfide, the person performing the operation should be informed of carbon disulfide's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid carbon disulfide may contact the eyes.

SANITATION

- Skin that becomes contaminated with carbon disulfide should be promptly washed or showered with soap or mild detergent and water to remove any carbon disulfide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon disulfide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of viscose rayon during xanthation of cellulose and spinning and cutting operations; use as a xanthating agent in manufacture of cellophane; use during manufacture of pesticides	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use as a fumigant and spray application on grains, and space fumigation of agricultural premises	General dilution ventilation; temperature control; personal protective equipment
Use in synthesis of carbon tetrachloride	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use in synthesis of intermediates and manufacture of dyes, pharmaceuticals, rubber chemicals, pesticides, and flotation agents	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Liberation during destructive distillation of coal in manufacture of coal gas and coal tar	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use as a solvent in dry spinning of polyvinyl chloride; as a solvent in oil wells; use in manufacture of optical glass	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use during rubber manufacture in cold curing operations; during extraction processing of oils, fats, resins, and waxes; use in manufacture of matches	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid carbon disulfide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid carbon disulfide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid carbon disulfide soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of carbon disulfide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid carbon disulfide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If carbon disulfide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Carbon disulfide should not be allowed to enter a confined space, such as

a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of carbon disulfide vapors are permitted.

- Waste disposal method:

Carbon disulfide may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR CARBON DISULFIDE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
200 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
500 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Carbon Monoxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CO
- Synonyms: Monoxide
- Appearance and odor: Colorless, odorless gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon monoxide is 50 parts of carbon monoxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 55 milligrams of carbon monoxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 35 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 200 ppm. The NIOSH Criteria Document for Carbon Monoxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon monoxide can affect the body if it is inhaled or if liquid carbon monoxide comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to carbon monoxide decreases the ability of the blood to carry oxygen to the tissues. Inhalation of carbon monoxide may cause headache, nausea, dizziness, weakness, rapid breathing, unconsciousness, and death. High concentrations may be rapidly fatal without producing significant warning symptoms. Exposure to this gas may aggravate heart disease and artery disease and may cause chest pain in those with pre-existing heart disease. Pregnant women are more susceptible to the effects of carbon monoxide exposure. The effects are also more severe in people who are working hard and in people who are working in places where the temperature is high or at altitudes above 2,000 feet. Skin exposure to liquid carbon monoxide may cause frostbite-type burns.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon monoxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to carbon monoxide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of coronary heart disease, anemia, pulmonary heart disease, cerebrovascular disease, thyrotoxicosis, and smokers would be expected to be at increased risk from exposure. Pregnant women have an increased sensitivity to the effects of carbon monoxide. Examination of the cardiovascular system, the pulmonary system, the blood, and the central nervous system should be stressed.

—A complete blood count: Carbon monoxide affects the ability of the blood to carry oxygen. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, with the exception that a carboxyhemoglobin determination should be performed at any time overexposure is suspected or signs or symptoms of toxicity occur.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Summary of toxicology**

Carbon monoxide (CO) gas causes tissue hypoxia by preventing the blood from carrying sufficient oxygen. CO combines reversibly with the oxygen-carrying sites on the hemoglobin molecule with an affinity ranging from 210 to 240 times greater than that of oxygen; the carboxyhemoglobin thus formed is unavailable to carry oxygen. In addition, carboxyhemoglobin interferes with the release of oxygen carried by unaltered hemoglobin. With exposure to high concentrations such as 4000 ppm and above, transient weakness and dizziness may be the only premonitory warnings before coma supervenes; the most common early aftermath of severe intoxication is cerebral edema. Exposure to concentrations of 500 to 1000 ppm causes the development of headache, tachypnea (rapid breathing), nausea, weakness, dizziness, mental confusion, and in some instances, hallucinations, and may result in brain damage. The affected person is commonly cyanotic. Concentrations as low as 50 ppm result in blood COHb levels up to 10% in an 8-hour day. This greatly increases the risk of angina pectoris and coronary infarctions by decreasing the oxygen supply in the blood and also in the myoglobin of the heart muscle. These effects are aggravated by heavy work, high ambient temperatures, and high altitudes. Pregnant women are especially susceptible to the effects of increased CO levels. Smoking also increases the risk: cigarette smoke contains 4% CO, which results in 5.9% COHb if a pack a day is smoked. The blood of persons not exposed to CO contains about 1% CO, probably as a result of normal heme metabolism. The diagnosis of CO intoxication depends primarily on the demonstration of significantly increased carboxyhemoglobin in the blood. Levels over 60% are usually fatal; 40% is associated with collapse and syncope; above 25% there may be electrocardiographic evidence of a depression of the S-T segment; between 15% and 25% there may be headache and nausea. The reaction to a given blood level of carboxyhemoglobin is extremely variable: some persons may be in coma with a carboxyhemoglobin level of 38% while others may maintain an apparently clear sensorium with levels as high as 55%. The blood of cigarette smokers contains 3 to 10% carboxyhemoglobin, and nonexposed persons have an average level of 1%, probably as a result of normal heme metabolism. Several investigators have suggested that the results of behavioral tests such as time discrimination, visual vigilance, choice response tests, visual evoked responses, and visual discrimination thresholds may be altered at levels of carboxyhemoglobin below 5%.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 28
2. Boiling point (760 mm Hg): −191.5 C (-313 F)
3. Specific gravity (water = 1): 0.79 (liquid at boiling point)
4. Vapor density (air = 1 at boiling point of carbon monoxide): 0.97
5. Melting point: −199 C (-326 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.004
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 609 C (1128 F)
3. Flammable limits in air, % by volume: Lower: 12.5; Upper: 74
4. Extinguishant: Dry chemical. If flow of gas cannot be stopped, let fire burn.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* points out that carbon monoxide is odorless.
2. Eye Irritation Level: Grant states that carbon monoxide is a non-irritating gas.
3. Evaluation of Warning Properties: Carbon monoxide is an odorless, non-irritating gas. It has no warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon monoxide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of carbon monoxide vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon monoxide may be used. An analytical method for carbon monoxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid carbon monoxide or from contact with vessels containing liquid carbon monoxide.
- Any clothing which becomes wet with liquid carbon monoxide should be removed immediately and not reworn until the carbon monoxide has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid carbon monoxide may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon monoxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from emissions in enclosed places from exhaust fumes of internal combustion engines; from metallurgic industry and foundries; from chemical industry for synthesis and emission as result of incomplete combustion	Local exhaust ventilation; respiratory protective device
Liberation during acetylene welding; from enclosed areas as mines or tunnels; from fire-damp explosions	Local exhaust ventilation; respiratory protective device
Liberation from industrial heating	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of carbon monoxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks or releases until cleanup has been completed.
- If carbon monoxide is leaked or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of leak or release to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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- American Conference of Governmental Industrial Hygienists: "Carbon Monoxide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Zenz, C.: *Occupational Medicine – Principles and Practical Applications*, Year Book Medical, Inc., Chicago, 1975.

RESPIRATORY PROTECTION FOR CARBON MONOXIDE

Condition	**Minimum Respiratory Protection* Required Above 50 ppm**
Gas Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against carbon monoxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON TETRABROMIDE

INTRODUCTION

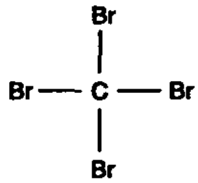
This guideline summarizes pertinent information about carbon tetrabromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CBr_4

- **Structure**



$$\begin{array}{ccc} & Br & \\ & | & \\ Br - & C & - Br \\ & | & \\ & Br & \end{array}$$

- **Synonyms**

  Carbon bromide, tetrabromomethane, methane tetrabromide

- **Identifiers**

  1. CAS No.: 558-13-4
  2. RTECS No.: FG4725000
  3. DOT UN: 2516 53
  4. DOT label: St. Andrew's Cross

- **Appearance and odor**

  Carbon tetrabromide is a nonflammable, colorless to yellow-brown, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 331.65
  2. Boiling point (760 mm Hg): 189.5°C (373.1°F)
  3. Specific gravity (water = 1): 3.42
  4. Vapor density (air = 1 at boiling point of carbon tetrabromide): 11.4
  5. Melting point: 90.1°C (194.2°F)
  6. Vapor pressure at 96.3°C (205°F): 40 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, chloroform, and other organic solvents
  8. Evaporation rate: Data not available

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Public Health Service
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National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: None reported
2. Incompatibilities: Contact of carbon tetrabromide with lithium or hexylcyclohexyldilead may cause an explosion.
3. Hazardous decomposition products: Toxic gases (such as bromine) may be released in a fire involving carbon tetrabromide.
4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to carbon tetrabromide; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or regular foam.

Fires involving carbon tetrabromide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbon tetrabromide. Structural firefighters' protective clothing may provide limited protection against fires involving carbon tetrabromide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for carbon tetrabromide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (1.4 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.3 ppm (4 mg/m^3) as a STEL. A STEL is a 15-min TWA exposure that should not be exceeded at any time during the workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbon tetrabromide a threshold limit value (TLV) of 0.1 ppm (1.4 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (4.1 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of eye, skin, lung, and liver irritation, and hepatotoxic effects associated with exposure to carbon tetrabromide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbon tetrabromide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbon tetrabromide is a severe irritant of the eyes and respiratory tract as well as a liver and kidney toxicant. Undiluted carbon tetrabromide applied to the eyes of rabbits caused severe irritation and permanent corneal damage. However, when the material was promptly washed from the eyes, pain and irritation were noted but the corneal damage was reversible. Exposure of rats to carbon tetrabromide fume at 10 mg/m^3 for 4 hr daily caused irritation of the eyes and respiratory tract [Clayton and Clayton 1981]. Contact with the skin of rabbits caused relatively slight irritation, but when the material was confined tightly to the skin, it caused hyperemia and a moderate degree of swelling [Clayton and Clayton 1981]. The subcutaneous LD$_{50}$ in mice is 298 mg/kg [NIOSH 1992b] and the rat oral

LD_{50} is 1,800 mg/kg [Clayton and Clayton 1981]. Rats exposed to 10 to 1,000 mg/m^3 (0.07 to 74 ppm) for 4 hr/day during a 4-month period exhibited metabolic changes in the liver [Clayton and Clayton 1981]. Rats repeatedly exposed to 100 mg/m^3 or to 300 to 500 mg/m^3 (depending on the analytical method) for 7 hr/day, 5 days/week during a 6-month period showed no effects, but exposure to higher (not further specified) concentrations caused poor growth; fatty and degenerative changes of the liver appeared at autopsy [Clayton and Clayton 1981].

2. *Effects on Humans:* Carbon tetrabromide is a severe irritant of the eyes, nose, throat, and lungs; it is also a liver toxicant. The vapor of carbon tetrabromide causes pronounced eye irritation and lacrimation even at low concentrations [Clayton and Clayton 1981]. Exposure to high concentrations (not further specified) of carbon tetrabromide vapors can irritate the upper respiratory tract, cause CNS depression, and injure the lungs, liver, and kidneys [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to carbon tetrabromide can induce corneal damage, profuse tearing and burning of the eyes; ocular, skin, and upper respiratory tract irritation; and CNS depression.

2. *Chronic exposure:* Liver damage is the primary response to chronic exposure to carbon tetrabromide at very low concentrations [Clayton and Clayton 1981]. Chronic exposure to low concentrations of carbon tetrabromide can also induce contact irritation.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritaiton!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of carbon tetrabromide. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbon tetrabromide or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

Workers may be exposed to carbon tetrabromide during its use as an intermediate in the manufacture of other chemicals.

The following methods are effective in controlling worker exposures to carbon tetrabromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbon tetrabromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and liver.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbon tetrabromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbon tetrabromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbon tetrabromide on the eyes, skin, and liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for carbon tetrabromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to carbon tetrabromide may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbon tetrabromide is determined by using an XAD-4 tube (80/40-mg sections, 15/50 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters (TWA) or 3 liters (STEL) is collected. The sample is then treated with toluene to extract the carbon tetrabromide. Analysis is conducted by gas chromatography using an electron capture detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If carbon tetrabromide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with carbon tetrabromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of carbon tetrabromide, particularly its potential to cause burns of the eyes and skin.

A worker who handles carbon tetrabromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbon tetrabromide or a solution containing carbon tetrabromide is handled, processed, or stored.

STORAGE

Carbon tetrabromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbon tetrabromide should be protected from physical damage and should be stored separately from strong oxidizers, lithium, hexylcyclohexyldilead, heat, sparks, and open flame. Because containers that formerly contained carbon tetrabromide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving carbon tetrabromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Use a clean shovel and gently place the spilled material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbon tetrabromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the National Response Center of an accidental release of carbon tetrabromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbon tetrabromide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbon tetrabromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbon tetrabromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, gauntlets, aprons, coveralls, and other clothing, as appropriate) should be worn to prevent any skin contact with carbon tetrabromide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. A Viton/neoprene laminate has been tested against carbon tetrabromide and has demonstrated good resistance. A laminate of butyl rubber and neoprene has demonstrated poor resistance to permeation by carbon tetrabromide.

If carbon tetrabromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbon tetrabromide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbon tetrabromide. Contact lenses should not be worn if the potential exists for carbon tetrabromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON TETRACHLORIDE

INTRODUCTION

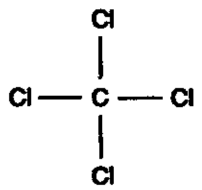
This guideline summarizes pertinent information about carbon tetrachloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CCl_4

- **Structure**



$$\begin{array}{c} Cl \\ | \\ Cl - C - Cl \\ | \\ Cl \end{array}$$

- **Synonyms**

Tetrachloromethane; perchloromethane; methane tetrachloride; Nectorina; benzinoform; carbon chloride; Carbona; carbon tet

- **Identifiers**

1. CAS No.: 56-23-5
2. RTECS No.: FG4900000
3. DOT UN: 1846 55
4. DOT label: Poison

- **Appearance and odor**

Carbon tetrachloride is a noncombustible, colorless liquid with a sweet, aromatic, etherlike odor. The best estimate of the odor threshold for carbon tetrachloride is 250 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 153.84
2. Boiling point (760 mm Hg): 76.7°C (170°F)
3. Specific gravity (water = 1): 1.59 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of carbon tetrachloride): 5.3
5. Melting point: −23°C (−9.4°F)
6. Vapor pressure at 20°C (68°F): 91.3 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; miscible with alcohol, benzene, chloroform, ether, carbon disulfide, petroleum ether, and oils

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of carbon tetrachloride with fluorine gas, alkali metals, or aluminum may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as phosgene and hydrogen chloride) may be released in a fire involving carbon tetrachloride. When used to put out electrical fires, carbon tetrachloride may evolve phosgene gas.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to carbon tetrachloride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is appropriate for the materials involved in the surrounding fire.

Fires involving carbon tetrachloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbon tetrachloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Fire fighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbon tetrachloride. Chemical protective clothing that is specifically recommended for carbon tetrachloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural Fire fighters' protective clothing is not effective against fires involving carbon tetrachloride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbon tetrachloride is 10 ppm as an 8-hr time-weighted average (TWA) concentration with a ceiling concentration of 25 ppm that may not be exceeded during an 8-hr workday except for a 5-min period every 4 hours; the acceptable maximum peak during this 5-min period is 200 ppm [29 CFR 1910.1000, Table Z-2].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) designates carbon tetrachloride a potential occupational carcinogen and has established a recommended exposure limit (REL) for this substance of 2 ppm (12.6 mg/m^3) as a 60-min short-term exposure limit (STEL) [NIOSH 1992a]. The STEL is a 60-min TWA exposure that shall not be exceeded at any time during a workday.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated carbon tetrachloride an A2 substance (suspected human carcinogen) and has assigned carbon tetrachloride a threshold limit value (TLV) of 5 ppm (31 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned carbon tetrachloride a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cancer associated with exposure to carbon tetrachloride [ACGIH 1993; NIOSH 1992a].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbon tetrachloride can occur through inhalation of the vapor, eye or skin contact, absorption through the skin of the liquid, or ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbon tetrachloride is an eye and skin irritant, a liver and kidney toxin, and a carcinogen. This chemical is a mild eye and skin irritant in rabbits [NIOSH 1992b]. Monkeys demonstrated little dermal absorption from ambient exposures. Likewise, rats dermally exposed to the liquid required large doses to induce lethality [Clayton and Clayton 1981]. The dermal LD_{50} in rats is 5,070 mg/kg [NIOSH 1992b]. The maximum exposures that caused no effects in male rats were: 3,000 ppm for 6 min, 800 ppm for 30 min, and 50 ppm for 7 hr [Clayton and Clayton 1981]. The highest airborne concentrations in which rats survived were 12,000 ppm for 15 min and 3,000 ppm for 8 hr [Clayton and Clayton 1981]. The LC_{50} in rats and mice are 8,000 ppm for 4 hr and 9,526 ppm for 8 hr, respectively [NIOSH 1992b]. The oral LD_{50} in rats is 2,350 mg/kg [NIOSH 1992b]. Rats, guinea pigs, rabbits, and monkeys were exposed to carbon tetrachloride vapors for 7 hr/day, 5 days/week for up to 4 months. Rats, guinea pigs, and rabbits all showed histologic damage to the liver after exposures of 10 ppm or higher but not after exposure to 5 ppm; monkeys exhibited histologic damage to the liver at concentrations of 100 ppm or above but not at lower levels [Clayton and Clayton 1981]. Carbon tetrachloride was embryotoxic and fetotoxic but not teratogenic in rats exposed to 300 to 1,000 ppm for 7 hr/day on days 6 to 15 of gestation [IARC 1979; NIOSH 1992b]. This chemical also increased fetal mortality when pregnant mice were given a single 150 mg dose [IARC 1979]. Carbon tetrachloride is weakly mutagenic in a wide variety of test systems [NIOSH 1992b]. This chemical produced liver tumors as well as cancers in mice, rats, and hamsters following administration by several routes, including inhalation and ingestion [ACGIH 1991; IARC 1979]. The International Agency for Research on Cancer (IARC) has determined that there is sufficient evidence of carbon tetrachloride's carcinogenicity in animals and that it is a Group 2B carcinogen (possibly carcinogenic in humans) [IARC 1987].

2. *Effects on Humans:* In humans, carbon tetrachloride is a mild eye and skin irritant, a central nervous system depressant, and a liver and kidney toxin. NIOSH, ACGIH, and other organizations classify carbon tetrachloride as a potential human carcinogen. The vapor of carbon tetrachloride is mildly irritating to the eyes [Grant 1986]; and has also caused visual disturbances (concentric restriction of color fields) [NLM 1991]. Prolonged or repeated contact of the liquid with the skin can cause pain, erythema, hyperemia, weal formation, tissue defatting and blistering [Grant 1986; Hathaway et al. 1991; NLM 1991]. The estimated no-observed-effect level for acute human exposure is 10 ppm for 3 hr [Hathaway et al. 1991]. A TC_{Lo} (lowest concentration causing an effect) exposure of 20 ppm (duration undefined) or 317 ppm for 30 min has produced nausea and vomiting [NIOSH 1992b]. Acute symptoms can include abdominal cramps, nervousness, dyspnea, cyanosis, oliguria, proteinuria, hepatomegaly, and optic neuritis [NIOSH 1992b]. Polycythemia, anemia, and hemodilution also may follow acute exposure [Hathaway et al. 1991]. Mild acute poisoning can result in renal injury, and decreased renal blood flow and filtration, which may require up to 200 days for complete recovery. In severe acute poisoning, anuria and terminal uremia require active restoration of renal function, or death occurs [NLM 1991]. In humans, the majority of fatalities caused by inhalation of carbon tetrachloride have been the result of renal injury with secondary cardiac failure. Liver damage occurs more often from ingestion of the liquid than from inhalation of the vapor [Hathaway et al. 1991]. Persons consuming alcohol, those with poor nutritional status, and persons with pre-existing liver or kidney disease are more susceptible to poisoning by carbon tetrachloride [Gosselin et al. 1984]. Human fatalities caused by acute renal failure have resulted from exposure to carbon tetrachloride concentrations of 50,000 ppm for 5 min [NLM 1991], 1,000 to 2,000 ppm for 30 min to 1 hr [Hathaway et al. 1991], or oral doses that exceed 1,500 mg/kg [NIOSH 1992b]. Although repeated exposure of workers to 10 ppm did not induce signs or symptoms of toxicity, 25 to 30 ppm caused nausea, vomiting, dizziness, drowsiness, and headache [NLM 1991]. Ten out of 17 workers exposed for an unspecified period to a 45- to 97-ppm concentration of carbon tetrachloride reported experiencing headache and giddiness, and several of these workers also had symptoms of liver dysfunction [ACGIH 1991]. Workers exposed to carbon tetrachloride at unspeci-

fied levels have experienced dizziness, vertigo, mental confusion, and incoordination, all signs and symptoms of central nervous system depression, and some have developed loss of visual acuity, convulsions, and cardiac arrhythmias [Hathaway et al. 1991]. Carbon tetrachloride has been confirmed as a weak mutagen in a variety of assays [NIOSH 1992b]. In the preamble of the 1989 *Air Contaminants; Final Rule,* OSHA concluded that an "occupational exposure to carbon tetrachloride at the 10-ppm PEL presents a significant risk of cancer to workers" [54 Fed. Reg. 2681 (1989)]. IARC has concluded that there is insufficient human data to directly classify carbon tetrachloride's carcinogenic risk to humans [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbon tetrachloride can induce mild irritation of the eyes and skin, with redness and inflammation, and central nervous system depression, with symptoms of malaise, headache, dizziness, incoordination, confusion, stupor, coma, and convulsions; nausea, vomiting, abdominal pain, and diarrhea are also frequent. Acute exposures can lead to ventricular fibrillation (rapid, irregular heartbeat) and death from cardiac failure. Acute oral exposures have primarily caused liver damage, as evidenced by an enlarged and tender liver and jaundice, as well as acute nephritis, with a decrease in the volume of urinary output and the presence of blood, pus, or protein in the urine. Acute renal failure can result in coma and death.

2. *Chronic exposure:* Repeated contact of the skin with carbon tetrachloride may cause defatting of the skin and dermatitis, with redness and blister formation. Chronic exposure has also been associated with nausea, vomiting, dizziness, drowsiness, headache, visual disturbances, and loss of visual acuity. The IARC classifies carbon tetrachloride as possibly carcinogenic to humans based on sufficient animal data.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of carbon tetrachloride. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbon tetrachloride or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by touching the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbon tetrachloride and result in worker exposures to this substance:

—Manufacture of fluorocarbons for aerosols, refrigerants, and fire extinguishants (these uses of fluorocarbons have been largely phased out or banned)

—Use as a solvent in dry cleaning and in industry to dissolve resins, oils, fats, varnishes, and rubber waxes

—Use as an agricultural grain fumigant, pesticide, and anthelmintic and as an agent to extract oil from flowers and seeds

—Use in polymer technology as a reaction medium, catalyst, and chain transfer agent

—Use in organic synthesis for the chlorination of organic compounds and in the soap and perfume industries

—Use as a laboratory solvent

—Use in tin recovery and catalyst regeneration and as a cleaning agent for machinery and electrical equipment

The following methods are effective in controlling worker exposures to carbon tetrachloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbon tetrachloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbon tetrachloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of excessive alcohol intake and other findings consistent with diseases of the liver, kidney, or nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbon tetrachloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbon tetrachloride on the liver, kidneys, or nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although carbon tetrachloride can be detected in the breath of exposed workers, data on the correlation between breath concentrations and airborne concentrations of carbon tetrachloride are not available. Therefore, no biological monitoring test acceptable for routine use has yet been developed for carbon tetrachloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to carbon tetrachloride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbon tetrachloride is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a maximum air volume of 15 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg, and the method is described in NIOSH Method No. 1003 [NIOSH 1984].

PERSONAL HYGIENE

This substance can be absorbed through the skin in toxic amounts. Therefore, if carbon tetrachloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with carbon tetrachloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbon tetrachloride, particularly its potential to cause severe central nervous system effects on acute exposure.

A worker who handles carbon tetrachloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbon tetrachloride is handled, processed, or stored.

STORAGE

Carbon tetrachloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbon tetrachloride should be protected from physical damage and direct sunlight and should be stored separately from aluminum, barium, dimethyl formamide, magnesium, potassium, sodium, triethylaluminum, calcium disilicide decaborane, ethylene, heat, sparks, and open flame. Because containers that formerly contained carbon tetrachloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbon tetrachloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.
4. Use water spray to reduce vapors.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the carbon tetrachloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbon tetrachloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbon tetrachloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of carbon tetrachloride per calendar year are required by EPA [49 CFR Part 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbon tetrachloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Carbon tetrachloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 355.40], and has been assigned EPA Hazardous Waste No. U211. This chemical is approved for land disposal as long as the concentration of carbon tetrachloride in the waste or treatment residual does not exceed 5.6 mg/kg. Carbon tetrachloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbon tetrachloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with carbon tetrachloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by carbon tetrachloride and may provide protection for periods greater than 8 hr: polyvinyl alcohol, Viton, Barricade®, and Responder®. Materials that may withstand permeation for more than 4 but fewer than 8 hr are Teflon and a polyethylene/ethylene vinyl laminate. Protective clothing made of butyl rubber, natural rubber, neoprene, nitrile rubber, polyethylene, or polyvinyl chloride are not recommended for protection against permeation by carbon tetrachloride.

If carbon tetrachloride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbon tetrachloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbon tetrachloride. Contact lenses should not be worn if the potential exists for carbon tetrachloride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBONYL FLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about carbonyl fluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CF_2O

- **Synonyms**

Carbon difluoride oxide, carbon fluoride oxide, carbon oxyfluoride, carbonyl difluoride, difluoroformaldehyde, fluoroformyl fluoride, fluorophosgene, carbonic difluoride

- **Identifiers**

1. CAS No.: 353-50-4
2. RTECS No.: FG6125000
3. DOT UN: 2417 15
4. DOT label: Poison Gas

- **Appearance and odor**

Carbonyl fluoride is a noncombustible, colorless, hygroscopic gas with a pungent and very irritating odor. It is shipped as a liquefied gas under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 66.01
2. Boiling point (760 mm Hg): -83°C (-117.6°F)
3. Specific gravity (water = 1): 1.14 at -114°C (-173°F)
4. Vapor density: Data not available
5. Melting point: -114°C (-173°F)
6. Vapor pressure at 21.1°C (70°F): 42,104 mm Hg
7. Solubility: Instantly hydrolyzed by water; decomposes in alcohol
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Contact with moisture causes the instantaneous hydrolysis of carbonyl fluoride to very corrosive and toxic hydrogen fluoride gas and carbon dioxide.

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases (such as oxides of fluorine and carbon) may be released in a fire involving carbonyl fluoride.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to carbonyl fluoride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical or carbon dioxide for small fires; water spray, fog, or regular foam for large fires.

Fires involving carbonyl fluoride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbonyl fluoride may explode in the heat of the fire and should be removed if it is possible to do safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do not get water inside the containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbonyl fluoride. Structural firefighters' protective clothing is not effective against fires involving carbonyl fluoride.

XPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) had not promulgated a permissible exposure limit (PEL) for carbonyl fluoride [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (5 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 5 ppm (15 mg/m^3) as a STEL. A STEL is a 15 min exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbonyl fluoride a threshold limit value (TLV) of 2 ppm (5.4 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 5 ppm (13 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of irritation associated with exposure to carbonyl fluoride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbonyl fluoride can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Carbonyl fluoride gas causes severe contact irritation or corrosion of tissues following acute exposure. In the presence of humidity or tissue fluids, it is rapidly hydrolyzed to two moles of hydrofluoric acid which is primarily responsible for the toxic effects elicited in exposed subjects. A near-lethal acute exposure, 310 ppm for 1 hr, of sacrificed mice, rats, guinea pigs, rabbits, and dogs resulted in the following histological lung changes: focal hemorrhage and edema at 24 hr; cellular repair with decreased edema at 48 hr; repair of damaged alveolar capillaries before 7 days; and a small amount of irreversible focal emphysema and mild interstitial fibrosis at the terminal 3-week sacrifice. The LC_{50}s in rats are 360 ppm for 1 hr and 90 ppm for 4 hr [NIOSH 1991]. Death resulted from respiratory or cardiac failure [NIOSH 1991; Scheel et al. 1968a]. Rats were exposed to polytetrafluoroethylene (PTFE) pyrolysis products containing hydrolyzable fluoride equal to a 50-ppm concentration of carbonyl fluoride for 1 hr/day for 5 days. Daily urinary fluoride levels reached 14 times normal on the first exposure day and continued to be markedly elevated 18 days after exposure. The animals' body weights declined by 30%, urinary glucose, protein, and ketones became

abnormal, and succinic-dehydrogenase activity declined sharply in the kidney and rose sharply in the lung. Mortality among the rats exposed repeatedly to carbonyl fluoride was high (9 of 40), indicating that fluoride continued to be liberated by hydrolysis once in the body [Scheel et al. 1968b].

2. *Effects on Humans:* Carbonyl fluoride is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans. Its respiratory toxicity is believed to be equivalent to that of hydrogen fluoride [ACGIH 1993]. On repeated exposure, carbonyl fluoride inhibits succinic dehydrogenase activity, indicating that sublethal exposures are cumulative and that fluoride continues to be liberated after absorption into the body [Sittig 1985].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbonyl fluoride can cause pain, redness, and tearing of the eyes, eye or skin burns (corrosion), runny nose, coughing, pulmonary edema, and difficult breathing.

2. *Chronic exposure:* Carbonyl fluoride toxicity is similar to that caused in fluoride poisoning: respiratory distress, neurological abnormalities, gastrointestinal pain, muscular fibrillation, and skeletal fluorosis (excessive calcification of bone).

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* Severe burns and skin corrosion may result! If tissue is frozen, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If tissue is not frozen, ***immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbonyl fluoride and may result in worker exposures to this substance:

—Use in organic synthesis

—Thermal decomposition of polytetrafluoroethylene (Teflon, Fluon, etc.)

—Proposed use as a military poison gas

The following methods are effective in controlling worker exposures to carbonyl fluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbonyl fluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, respiratory system, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbonyl fluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbonyl fluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbonyl fluoride on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary fluoride concentration is a useful index of fluoride intake in workers; at an airborne concentration of 2.5 g/m^3 inorganic fluoride, average end-of-shift (8 hr) urinary concentrations are 4 mg fluoride per liter of urine. Some sources recommend an end-of-shift biological exposure index (BEI) of 10 mg fluoride per gram creatinine and a preshift BEI of 3 mg fluoride per gram creatinine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbonyl fluoride is determined by using a midget fritted-glass bubbler containing 10 ml 0.1N sodium hydroxide. Samples are collected at a recommended flow rate of 2.0 liter/min until a recommended air volume of 480 liters is collected. Analysis is conducted using an ion specific electrode. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If carbonyl fluoride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with carbonyl fluoride should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles carbonyl fluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbonyl fluoride is handled, processed, or stored.

STORAGE

Carbonyl fluoride should be stored in a cool, dry, well-ventilated area in tightly sealed, pressurized containers or holding tanks that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All piping systems in storage areas should be equipped with leak detection equipment to provide warning of leaks. Containers of carbonyl fluoride should be protected from physical damage and should be stored separately from moisture and heat.

LEAKS

In the event of a leak involving carbonyl fluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the leak.
5. For small spills, flush area with flooding amounts of water.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbonyl fluoride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbonyl fluoride is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

Community right-to-know requirements

Employers are not required by Section 313 of SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbonyl fluoride emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Carbonyl fluoride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U033. This substance has been banned from land disposal and may be treated by incineration. Carbonyl fluoride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbonyl fluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, boots, aprons, and gauntlets) should be worn to prevent any skin contact with carbonyl fluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to carbonyl fluoride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to carbonyl fluoride.

Safety glasses, goggles, or face shields should be worn during operations in which carbonyl fluoride might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbonyl fluoride. Contact lenses should not be worn if the potential exists for carbonyl fluoride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CATECHOL

INTRODUCTION

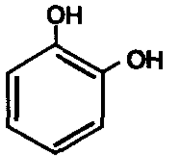
This guideline summarizes pertinent information about catechol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_4(OH)_2$

- **Structure**



- **Synonyms**

1,2-Benzenediol; pyrocatechol; o-dihydroxybenzene; pyrocatechin; o-diphenol; Durafur Developer C; o-hydroquinone; o-hydroxyphenol; oxyphenic acid; Pelagol Grey C; o-phenylenediol; pyrocatechinic acid

- **Identifiers**

1. CAS No.: 120-80-9
2. RTECS No.: UX1050000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Catechol is a colorless, crystalline solid that has a faint odor and sublimes easily.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110.11
2. Boiling point (760 mm Hg): 245.5°C (473.9°F)
3. Specific gravity (water = 1): 1.344 at 40°C (104°F)
4. Vapor density (air = 1 at boiling point of catechol): 3.79
5. Melting point: 105°C (221°F)
6. Vapor pressure at 118°C (244°F): 10 mm Hg
7. Solubility: Soluble in water, ether, alcohol, hot benzene, and chloroform; very soluble in pyridine and acetone

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8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, flame, light, or air

2. Incompatibilities: Contact of catechol with strong oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving catechol.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to catechol; other sources rate catechol's fire hazard as slight.

1. Flash point: 127.2°C (261°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use water, dry chemical, or carbon dioxide to fight fires involving catechol.

Fires involving catechol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving catechol.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for catechol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (20 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned catechol a threshold limit value (TLV) of 5 ppm (20 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of skin and respiratory tract irritation and central nervous system effects associated with exposure to catechol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to catechol can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Catechol is a potential corrosive to the eyes, nose, upper respiratory tract, and skin. Aqueous solutions of up to 55% (0.05 M) were not injurious when instilled into rabbits' eyes [Grant 1986]. Application of 100 mg of dry catechol onto rabbits' eyes caused erythematous and edematous conjunctiva, moderate exudate, and corneal opacities (Draize score 103/110) within 24 hr. The 72-hr evaluation revealed severe conjunctivitis, iritis, and diffuse corneal opacities (Draize score 78/110). On the 14th day, corneal vascularization, granulation, and conical protrusion were observed [Flickinger 1976]. Administration of catechol onto rabbit skin produced moderate erythema and slight edema of the intact sites while necrosis occurred at the abraded areas. Catechol was thereby classified as a primary irritant (Draize score 5.5/8.0) [Flickinger 1976]. The dermal LD$_{50}$ in the rabbit is 800 mg/kg [NIOSH 1992b]. Rats tolerated an 8-hr inhalation exposure to 1,500 mg/m^3 catechol without visible effects, but exposure to 2,000 or 2,800 mg/m^3 caused tremors after 6 to 7 hr. The tremors disappeared following the first experimental day. In addition, the 2,000- and 2,800-mg/m^3

concentrations caused the animals to develop irritated and blackened extremities and tails. Two of six rats exposed to 2,000 mg/m^3 developed blackened tails of which the terminal one inch was lost (undefined). Six out of six rats exposed to 2,800 mg/m^3 had both blackened tails and toes. All lost the terminal inch of their tails, while several had missing toes. The author concluded that severe exposure could lead to necrosis and sloughing of peripheral tissues [Flickinger 1976]. Lethal oral doses have induced hyperemia of the stomach and intestines of rats [Clayton and Clayton 1981]. The lowest reported oral LD_{50}s for the rat and mouse are 260 and 260 mg/kg, respectively [NIOSH 1992b]. Large doses (amounts not specified) of catechol can cause depression of the central nervous system, a prolonged rise in blood pressure, and degenerative changes in the renal tubules. Deaths from lethal doses or exposures in animals are caused from respiratory failure [Clayton and Clayton 1981; ACGIH 1991]. Rabbits that received repeated sublethal oral doses (200 mg/kg) had altered sleep times, leukopenia, anemia, and methemoglobinemia [Clayton and Clayton 1981; NIOSH 1992b]. An in vitro micromass teratogen test confirmed that catechol inhibits cell differentiation of rat embryo midbrain and limb cells [Flint and Maclean 1988]. Conversely, in an in vivo Chernoff/Kavlock assay, rats received one oral dose of 333, 667, or 1,000 mg catechol/kg on day 11 of pregnancy. The lethality rates in dams were 1/15, 5/15, and 10/15, respectively. The two upper levels caused a statistically significant dose-related decrease in litter size and an increase in perinatal loss. The 333-, 667-, and 1,000-mg/kg dose levels induced a 23.1%, 66.7%, and 80% incidence of hind limb tetany and paralysis, short or kinky tails, and urogenital malformations in the pups, respectively [Kavlock 1990]. Catechol is mutagenic in bacterial and mammalian test systems [NIOSH 1992b]. Groups of 50 Swiss mice received 5 g benzo(a)pyrene [B(a)P] with or without 2-mg catechol in acetone, three times per week for 52 weeks. Catechol plus B(a)P significantly increased the number of squamous cell carcinomas of the skin (31) when compared to benzo(a)pyrene alone (10), acetone controls (0), or negative controls (0). The rate of skin papillomas per affected mouse was also tripled when catechol plus B(a)P were administered. Catechol alone was not investigated in this study [IARC 1977]. When 2-mg catechol were suspended in 10-mg cholesterol pellets and implanted into the urinary bladders of mice for 25 weeks, a significant increase ($p=0.03$) in undefined carcinomas was induced above the control incidence [IARC 1977]. IARC found no adequate human studies and inadequate evidence of carcinogenic potential for the above animal studies. They classified it as a Group 3 chemical: The agent is not classifiable as to its carcinogenicity to humans [IARC 1977].

2. *Effects on Humans:* In humans, catechol is an eye and skin irritant, a skin sensitizer, and a depressant of the central nervous system. Catechol also causes eye burns that are slow to heal [Grant 1986]. Contact of catechol with the skin causes an eczematous dermatitis in sensitized workers. Absorption through the skin has resulted in signs and symptoms of illness resembling those of phenol poisoning, except that catechol-induced convulsions are more severe than those caused by phenol poisoning [ACGIH 1991]. Catechol is mutagenic in human test systems [NIOSH 1992b].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to catechol can cause redness, pain, and tearing of the eyes, runny nose, scratchy throat, and difficult breathing. Contact of catechol with the eyes may cause burns and permanent impairment of vision. Severe overexposure may cause convulsions.

2. *Chronic exposure:* Continued low-level exposure to catechol can cause eczematous dermatitis, with red, raised, and oozing areas of the skin.

- **Emergency Procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* If particulates, mists, or vapors of catechol are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if catechol or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve catechol and result in worker exposures to this substance:

—Use as an intermediate in the manufacture of 4-tertiary-butyl-catechol and certain chlorinated dibenzo-para-dioxins

—Use as a constituent of polymerization inhibitors and antioxidants

—Use in electro-sensitive copying papers, in photography, and in rubber compounding

—Use as a photographic developer, as an oxidation base in hair dye preparations, and as an analytical reagent

—Use as an antiseptic

—Use in the manufacture of specialty inks and light stabilizers

The following methods are effective in controlling worker exposures to catechol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to catechol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to catechol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory system or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to catechol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of catechol on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although catechol can be measured in the urine of exposed individuals, no correlation between urinary and airborne catechol concentrations has yet been established. Therefore, no biological monitoring test acceptable for routine use is available for catechol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne catechol is determined by using an XAD-7 tube (100/50-mg sections, 15/50 mesh). Samples are collected at a recommended flow rate of 0.1 liter/min until a recommended air volume of 24 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If catechol contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with catechol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of catechol, particularly its potential to cause eye and skin burns on contact.

A worker who handles catechol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where catechol or a solution containing catechol is handled, processed, or stored.

STORAGE

Catechol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of catechol should be protected from physical damage and should be stored separately from strong oxidizers, light, heat, sparks, and open flame. Because containers that formerly contained catechol may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving catechol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Avoid raising dust during cleanup.
6. Sweep or vacuum the spilled material and gently place into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Catechol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of catechol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or otherwise use 10,000 lb or more of catechol per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of catechol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although catechol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of catechol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with catechol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to catechol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to catechol.

If catechol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which catechol might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with catechol. Contact lenses should not be worn if the potential exists for catechol exposure.

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Kavlock RJ [1990]. Structure-activity relationships in the developmental toxicity of substituted phenols: in vivo effects. Teratology 41(1):43-59.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CELLULOSE

INTRODUCTION

This guideline summarizes pertinent information about cellulose for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$(C_6H_{10}O_5)_n$

- **Synonyms**

Abicel; β-Amylose; Avicel; α-Cellulose; Cellex MX; Arbocel; Cupricellulose; Cellulose 248; Hydroxycellulose; Pyrocellulose; Sulfite cellulose

- **Identifiers**

1. CAS No.: 9004-34-6
2. RTECS No.: FJ5691460
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Cellulose is the principal fiber cell wall material of green terrestrial and marine plants; it is the most abundant polysaccharide produced in nature. Cellulose is a white substance that is odorless and tasteless. Natural cellulose exists both in microcrystalline and nonfibrous forms.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 300,000 to greater than 1,000,000 depending on the degree of polymerization of the particular cellulose
2. Boiling point: Not applicable
3. Specific gravity (water = 1): 1.27 to 1.61
4. Vapor density: Not applicable
5. Melting point: 260° to 270°C (500° to 518°F) (decomposes)
6. Vapor pressure: Not applicable
7. Solubility: Insoluble in water and organic solvents; dissolved by concentrated zinc chloride solutions, by ammoniacal copper hydroxide solutions, and by caustic alkali with carbon disulfide
8. Evaporation rate: Not applicable

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- **Reactivity**

1. Conditions contributing to instability: Heat or moisture

2. Incompatibilities: Contact of cellulose with water, bromine pentafluoride, sodium nitrate, or fluorine may cause fires and violent explosions.

3. Hazardous decomposition products: Toxic gases and particulates (such as carbon monoxide and carbon dioxide) may be released in a fire involving cellulose.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to cellulose; however, cellulose is combustible and may be flammable under certain conditions.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use water to fight fires involving cellulose.

Fires involving cellulose should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cellulose.

XPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cellulose is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cellulose (total dust) a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of local irritant effects associated with exposure to cellulose.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cellulose can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* There are no acute or chronic toxicity studies in animals for cellulose.

2. *Effects on Humans:* Like all dusts, cellulose dust produces mechanical irritation of the eyes, skin, or mucous membranes if it contacts these tissues in excessive amounts; there are no reports of other exposure-related effects of cellulose in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to cellulose, other than those of local irritation, have been reported.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to cellulose have been reported.

- **Emergency procedures**

WARNING

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.
2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.
3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.
4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of cellulose is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.
5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cellulose and may result in worker exposures to this substance:

—Manufacture of paper, fillers, cellophane, and rayon in the textile and paper industries

—Production of chemical derivatives such as certain explosives

—Use as a source of ethanol (enzymatic hydrolysis) and methanol (destructive distillation of wood)

—Use in the food industry to produce stabilizers, thickeners, and texturizers and in fillings and meringue

—Generated during wood processing and logging

The following methods are effective in controlling worker exposures to cellulose, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cellulose, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cellulose at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cellulose exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cellulose on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cellulose.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cellulose (total dust) is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5 microns). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by the gravimetric (weighing) method. This method has a sampling and analytical error of 0.10 and is described in the OSHA Computerized Information System [OSHA 1989], the *OSHA Chemical Information Manual* [OSHA 1987], and in NIOSH Method No. 0500 in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

A worker's exposure to airborne cellulose (respirable fraction) is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5 microns) preceded by a 10-mm nylon cyclone. Samples are collected at a maximum flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by the gravimetric (weighing) method. This method has a sampling and analytical error of 0.10 and is described in the OSHA Computerized Information System, the *OSHA Chemical Information Manual*, and in NIOSH Method No. 0600 in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If a large amount of cellulose dust collects on the skin, workers should wash the affected areas with soap and water.

Clothing excessively contaminated with cellulose should be removed to avoid local irritation of the skin.

A worker who handles cellulose should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cellulose is handled, processed, or stored.

STORAGE

Cellulose should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of cellulose should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving cellulose, the following steps should be undertaken: use a clean shovel and place the material into a clean, dry container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cellulose is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cellulose; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cellulose emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cellulose is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cellulose exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged contact of the skin with cellulose dust. Safety glasses, goggles, or face shields should be worn during operations in which cellulose might contact the eyes (e.g., through dust particles).

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CESIUM HYDROXIDE

INTRODUCTION

This guideline summarizes pertinent information about cesium hydroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CsOH$

- **Synonyms**

  Cesium hydrate; cesium hydroxide dimer; cesium hydroxide, solid; cesium hydroxide, solution

- **Identifiers**

1. CAS No.: 21351-79-1
2. RTECS No.: FK9800000
3. DOT UN: 2682 60 (solid); 2681 60 (solution)
4. DOT label: Corrosive

- **Appearance and odor**

  Cesium hydroxide is a noncombustible, colorless or yellowish, deliquescent, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 149.92
2. Boiling point: Data not available
3. Specific gravity (water = 1): 3.68
4. Vapor density: Data not available
5. Melting point: 272.3°C (522.1°F)
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Very soluble in water (generates heat); soluble in alcohol
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Cesium hydroxide is a strong base; in contact with water or moisture, it causes the generation of considerable heat.
2. Incompatibilities: Contact of cesium hydroxide with

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

acids, many organic compounds, many metals (such as aluminum, lead, tin, or zinc), glass, oxygen, or carbon dioxide causes a violent reaction.

3. Hazardous decomposition products: None reported

4. Special precautions: Cesium hydroxide must be stored in silver or platinum and out of contact with air because of its reactivity with glass and carbon dioxide.

Flammability

The National Fire Protection Association has not assigned a flammability rating for cesium hydroxide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to extinguish fires involving cesium hydroxide.

Fires involving cesium hydroxide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cesium hydroxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cesium hydroxide. Structural firefighters' protective clothing may provide limited protection against fires involving cesium hydroxide.

XPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cesium hydroxide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cesium hydroxide a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of eye irritation associated with exposure to cesium hydroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cesium hydroxide can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cesium hydroxide is irritating and corrosive to the eyes, mucous membranes, skin, and upper respiratory tract; the severity of these effects depends on the concentration of cesium hydroxide. Application of 5 mg cesium hydroxide to the eye of rabbits for 5 min, followed by rinsing with water, caused severe eye irritation; application of 5 mg to the skin of rabbits for 24 hr caused mild skin irritation [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50} for cesium hydroxide in the rat is 570 mg/kg, and the intraperitoneal LD_{50} in the same species is 100 mg/kg [NIOSH 1993]. The oral LD_{50} in mice is 800 mg/kg [NIOSH 1993; Sax and Lewis 1989; ACGIH 1991].

2. *Effects on Humans:* In humans, cesium hydroxide is irritating and corrosive to the eyes, nose, throat, and skin. Solutions containing 5% cesium hydroxide are regarded as safe for human skin contact; however, in contact with the eyes, a solution of this concentration causes extreme irritation and corneal corrosion [Sittig

1985]. Stronger solutions of cesium hydroxide cause eye and skin burns and may cause permanent damage. There is no other toxicological information on the effects of exposure to cesium hydroxide in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation exposure to cesium hydroxide include a burning sensation in nose, throat, and upper respiratory tract; runny nose; pain, redness and tearing of the eyes; difficult breathing; and redness, pain, and burns of the skin.

2. *Chronic exposure:* No signs or symptoms of continued low-level exposure to cesium hydroxide have been reported.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately*** but ***gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cesium hydroxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

   NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve cesium hydroxide and may result in worker exposures to this substance:

—Use as an electrolyte in alkaline storage batteries at subzero temperatures

—Use as a polymerization catalyst for siloxanes

—Use as an agent in the removal of sulfur from heavy oils

—Use as a raw material in the production of cesium salts, which are then used to produce cesium metal for electronic devices

The following methods are effective in controlling worker exposures to cesium hydroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cesium hydroxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cesium hydroxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cesium hydroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cesium hydroxide on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cesium hydroxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cesium hydroxide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Elemental cesium analysis is conducted by atomic absorption spectroscopy, and the results are reported as cesium hydroxide. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cesium hydroxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cesium hydroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cesium hydroxide, particularly its potential to cause eye and skin burns.

A worker who handles cesium hydroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cesium hydroxide or a solution containing cesium hydroxide is handled, processed, or stored.

STORAGE

Cesium hydroxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cesium hydroxide should not be stored in glass containers. Containers of cesium hydroxide should be protected from physical damage and should be stored separately from acids, organic compounds, metals, oxygen, carbon dioxide, moisture, heat, sparks, and open flame. Because containers that formerly contained cesium hydroxide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cesium hydroxide or a solution containing cesium hydroxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Do not use water in clean-up.
4. For small dry spills, use a scoop or clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
5. For liquid spills, dilute the concentration of cesium hydroxide with water, neutralize the spilled material with dilute acid, absorb with sand or other noncombustible absorbent material, and place into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

Emergency planning requirements

Cesium hydroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

Reportable quantity requirements for hazardous releases

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cesium hydroxide; there is no reportable quantity for this substance.

Community right-to-know requirements

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cesium hydroxide emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cesium hydroxide is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. D002. This substance has been banned from land disposal and may be treated by deactivation.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cesium hydroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cesium hydroxide. Rubber gloves, rubber aprons, or protective suits and rubber boots should be worn when needed to prevent contact with cesium hydroxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cesium hydroxide permeation; however, neoprene and polyvinyl-chloride have been tested against chemically similar materials (sodium hydroxide and potassium hydroxide) and may provide greater than 8-hr of resistance to permeation. Since specific test data are not available for cesium hydroxide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cesium hydroxide.

If cesium hydroxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cesium hydroxide might contact the eyes (e.g., through splashes of solutions containing cesium hydroxide). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cesium hydroxide. Contact lenses should not be worn if the potential exists for cesium hydroxide exposure.

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Occupational Health Guideline for Chlordane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_6Cl_8$ (approx.)
- Synonyms: 1,2,4,5,6,7,8,8-Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane; 1,2,4,5,6,7,8,8-octachloro-2,3, 3a,4,7,7a-hexahydro-4,7-methanoindene
- Appearance and odor: Thick amber liquid with a characteristic chlorine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlordane is 0.5 milligram of chlordane per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlordane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to chlordane may cause shaking, blurred vision, irritability, confusion, delirium, staggering, convulsions, and death. Swallowing chlordane may also cause nausea, vomiting, and diarrhea. Chlordane exposure may cause kidney and liver damage. Absorption of chlordane through the skin is rapid and has resulted in death.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlordane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlordane at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders would be expected to be at increased risk from exposure. Examination of the nervous system, eyes, lungs, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to chlordane, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chlordane predominantly affects the central nervous system, causing irritability, tremors, and convulsions. Chronic effects are reported in animals. Repeated oral administration to rabbits indicated a cumulative action at daily doses above 5 mg/kg; autopsy revealed focal necrosis of the liver, degenerative changes in the proximal convoluted tubules, pulmonary exudates and gastrointestinal irritation. In humans, inhalation and skin absorption have resulted in blurred vision, cough, confusion, ataxia, and delirium; ingestion has caused abdominal pain, nausea, vomiting, and diarrhea; severe intoxication has caused irritability, tremor, convulsions, and death. A suicidal person who ingested 6 g (104 mg/kg) of chlordane in talc suffered burns of the mouth, severe gastritis, diffuse pneumonia, anuria, mania, and convulsions; death occurred after 9.5 days; autopsy findings were severe necrotizing bronchopneumonia

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and degeneration of renal tubule epithelium. Skin absorption of chlordane is rapid; a worker who spilled a 25% suspension of chlordane on clothing, which was not removed, began having convulsions 40 minutes later and died shortly thereafter. Technical-grade chlordane is stated to be irritating to the skin and mucous membranes, but this may be due to the presence of unreacted chemical intermediates.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 409.8 (approx).
2. Boiling point (760 mm Hg): (Decomposes); 175 C (347 F) (at 2 mm Hg)
3. Specific gravity (water = 1): 1.57 — 1.67
4. Vapor density (air = 1 at boiling point of chlordane): 14
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 0.00001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 200 C (392 F) cause decomposition with formation of chlorine and hydrogen chloride gases.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when chlordane decomposes.
4. Special precautions: Chlordane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Since chlordane has such a low vapor pressure, warning properties are not considered. Grant describes certain effects produced by chlordane on the eyes, but these effects were caused by systemic poisoning. They were not local effects. Chlordane is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for chlordane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with chlordane.
- If employees' clothing has had any possibility of being contaminated with chlordane, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with chlordane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlordane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlordane, the person performing the operation should be informed of chlordane's hazardous properties.
- Where there is any possibility of exposure of an employee's body to chlordane, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chlordane should be removed immediately and not reworn until the chlordane is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where chlor-

dane may contact the eyes.

SANITATION

- Skin that becomes contaminated with chlordane should be immediately washed or showered with soap or mild detergent and water to remove any chlordane.
- Workers subject to skin contact with chlordane should wash with soap or mild detergent and water any areas of the body which may have contacted chlordane at the end of each work day.
- Eating and smoking should not be permitted in areas where chlordane is handled, processed, or stored.
- Employees who handle chlordane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlordane may occur and control methods which may be effective in each case:

Operation	Controls
Application as an insecticide on pre-planting soil, fire ants, and harvester ants (banned by EPA in 1976)	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlordane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlordane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlordane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of chlordane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlordane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlordane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Chlordane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR CHLORDANE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. A chin-style or front- or back-mounted pesticide gas mask. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode. A powered chemical cartridge respirator with an organic vapor cartridge and a high efficiency filter, including pesticide respirators which meet the requirements of this class.
Greater than 500 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlordane; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorinated Camphene*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_{10}Cl_8$ (average)
- Synonyms: Toxaphene
- Appearance and odor: Waxy, amber-colored solid with a mild, turpentine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorinated camphene is 0.5 milligram of chlorinated camphene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorinated camphene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin. It may enter the body through the skin.

- **Effects of overexposure**

Overexposure to chlorinated camphene may cause nausea, mental confusion, agitation, involuntary trembling, convulsions, and unconsciousness. Contact with chlorinated camphene solutions may cause irritation of the skin.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorinated camphene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorinated camphene at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system and the skin should be stressed. The skin should be examined for evidence of chronic disorders.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chlorinated camphene is primarily a strong stimulant to the central nervous system. Most fatal cases of poisoning have been due to accidental ingestion, resulting in convulsions, loss of consciousness, and respiratory failure. The minimal acute lethal oral dose for man is 2 to 7 g. Few cases of intoxication due to occcupational exposure have been reported. Two cases of pneumonitis in insecticide sprayers using chlorinated camphene in an emulsion containing kerosene and xylene have been reported, but the significance of this finding is questionable as it relates to the toxicity of chlorinated camphene exposure. In solution, the substance is absorbed through the skin and causes skin irritation. In man, a single dermal application of 46 grams, or daily application of 2.4 grams, is very dangerous. Animals given repeated oral doses show degenerative changes in the liver and kidneys. Chronic exposure results in the accumulation of the substance in the fatty tissues. It is metabolized in the liver and excreted in the urine, probably in a conjugated form. Laboratory testing has indicated that this substance causes cancer in laboratory animals.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 414 (average)
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.63
4. Vapor density (air = 1 at boiling point of chlorinated camphene): 14.3
5. Melting point: 70 to 95 C (158 to 203 F)
6. Vapor pressure at 20 C (68 F): 0.2 to 0.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0003
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, especially when in contact with iron.
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorinated camphene.
4. Special precautions: Emulsifiable concentrates of chlorinated camphene in xylene may decompose with liberation of much heat if allowed to come in contact with iron or aluminum above 70 C (158 F).

- **Flammability**

1. Flash point: 135 C (275 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, carbon dioxide

- **Warning properties**

Chlorinated camphene is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorinated camphene on a filter, followed by extraction with petroleum ether, and gas chromatographic analysis. An analytical method for chlorinated camphene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquids containing chlorinated camphene and to prevent repeated or prolonged skin contact with solid chlorinated camphene.
- If employees' clothing may have become contaminated with solid chlorinated camphene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with solid chlorinated camphene or liquids containing chlorinated camphene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorinated camphene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorinated camphene, the person performing the operation should be informed of chlorinated camphene's hazardous properties.
- Where exposure of an employee's body to liquids containing chlorinated camphene may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with solid chlorinated camphene should be removed promptly and non-impervious clothing which becomes contaminated with liquids containing chlorinated camphene should be removed immediately and such clothing should not be reworn until the chlorinated camphene is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

chlorinated camphene or liquids containing chlorinated camphene may contact the eyes.

SANITATION

- Skin that becomes contaminated with solid chlorinated camphene should be promptly washed or showered and skin that becomes contaminated with liquids containing chlorinated camphene should be immediately washed or showered with soap or mild detergent and water to remove any chlorinated camphene.
- Eating and smoking should not be permitted in areas where solid chlorinated camphene or liquids containing chlorinated camphene are handled, processed, or stored.
- Employees who handle solid chlorinated camphene or liquids containing chlorinated camphene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorinated camphene may occur and control methods which may be effective in each case:

Operation	Controls
Mixing and formulation of liquid, dust, powder, and granular insecticides	Personal protective equipment
Use in application of liquid, dust, powder, or granular insecticide formulations	Personal protective equipment
Manufacture and packaging of chlorinated camphene	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorinated camphene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorinated camphene gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If liquids containing chlorinated camphene get on the skin, immediately wash the skin using soap or mild detergent. If liquids containing chlorinated camphene soak through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent.

- **Breathing**

If a person breathes in large amounts of chlorinated camphene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlorinated camphene has been swallowed, get medical attention immediately. If the chlorinated camphene is dissolved in a petroleum-based material, do not make the exposed person vomit. If medical attention is not immediately available and the chlorinated camphene is a powder or in a water base, get the person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorinated camphene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, use a procedure similar to that for small quantities.

- Waste disposal methods:

Chlorinated camphene may be disposed of:

1. By making packages of chlorinated camphene in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving chlorinated camphene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with afterburner and scrubber (alkali).

ADDITIONAL INFORMATION

To find additional information on chlorinated camphene, look up chlorinated camphene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR CHLORINATED CAMPHENE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Vapor Concentration	
5 mg/m³ or less	Any pesticide chemical cartridge respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any pesticide chemical cartridge respirator with a full facepiece. A chin-style or front- or back-mounted pesticide gas mask. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A powered air-purifying pesticide respirator. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorinated camphene; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorinated Diphenyl Oxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_4Cl_6O$
- Synonyms: Hexachlorodiphenyl oxide
- Appearance: Waxy solid or liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorinated diphenyl oxide is 0.5 milligram of chlorinated diphenyl oxide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorinated diphenyl oxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Exposure to chlorinated diphenyl oxide may cause an acne-like skin eruption or irritation. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorinated diphenyl oxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorinated diphenyl oxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Chlorinated diphenyl oxide may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chlorinated diphenyl oxide vapor causes an acne-form dermatitis (chloracne). In laboratory animals, cumulative liver damage has resulted from repeated bodily intake and, in general, the toxicity increases with the degree of chlorination; in guinea pigs, a single oral dose of .05 to 0.1 g/kg of material containing 4 or more equivalents of chlorine resulted in death 30 days after administration. Limited experience with humans has shown that exposure to even small amounts of the higher chlorinated derivatives may result in appreciable acne-form dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 377
2. Boiling point (760 mm Hg): 230 to 260 C (446 to 500 F)
3. Specific gravity (water = 1): 1.60
4. Vapor density (air = 1 at boiling point of chlorinated diphenyl oxide): 13
5. Melting point: Data not available

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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6. Vapor pressure at 20 C (68 F): Less than 0.00006 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 0.1

8. Evaporation rate (butyl acetate = 1): Not available

- **Reactivity**

1. Conditions contributing to instability: Heat.

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorinated diphenyl oxide.

4. Special precautions: None.

- **Flammability**

1. Flash point: None

2. Autoignition temperature: 627 C (1163 F)

3. Flammable limits in air, % by volume: Not available

4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

Since there are no quantitative data relating warning properties to air concentrations of chlorinated diphenyl oxide, this material is treated as a substance with poor warning properties. The concentration of chlorinated diphenyl oxide in saturated air at 20 C could result in a significant exposure relative to the permissible exposure. There is no available information which indicates that chlorinated diphenyl oxides produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorinated diphenyl oxide on a filter with subsequent extraction with iso-octane and gas chromatographic analysis. An analytical method for chlorinated diphenyl oxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with chlorinated diphenyl oxide.
- If employees' clothing may have become contaminated with chlorinated diphenyl oxide, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with chlorinated diphenyl oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorinated diphenyl oxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorinated diphenyl oxide, the person performing the operation should be informed of chlorinated diphenyl oxide's hazardous properties.
- Non-impervious clothing which becomes contaminated with chlorinated diphenyl oxide should be removed promptly and not reworn until the chlorinated diphenyl oxide is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where chlorinated diphenyl oxide may contact the eyes.

SANITATION

- Workers subject to skin contact with chlorinated diphenyl oxide should wash with soap or mild detergent and water any areas of the body which may have contacted chlorinated diphenyl oxide at the end of each work day.
- Skin that becomes contaminated with chlorinated diphenyl oxide should be promptly washed or showered with soap or mild detergent and water to remove any chlorinated diphenyl oxide.
- Eating and smoking should not be permitted in areas where chlorinated diphenyl oxide is handled, processed, or stored.

- Employees who handle chlorinated diphenyl oxide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorinated diphenyl oxide may occur and control methods which may be effective in each case:

Operation	Controls
Use as intermediate in organic synthesis in manufacture of flame-inhibiting polymers; corrosion inhibitors, dry cleaning detergents, thermal lubricants, additives for soaps and lotions, manufacture of hydraulic fluids, pesticides, wood preservatives, and electric insulators (Literature review suggests that this compound is of little or no industrial significance).	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorinated diphenyl oxide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorinated diphenyl oxide gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid chlorinated diphenyl oxide or liquids containing chlorinated diphenyl oxide soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorinated diphenyl oxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlorinated diphenyl oxide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorinated diphenyl oxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, small quantities may be swept onto paper or other suitable material, placed in an appropriate container and burned in a safe place (such as a fume hood). Larger quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
4. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Chlorinated diphenyl oxide may be disposed of:

1. If in the solid form, by making packages of chlorinated diphenyl oxide in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device, or by dissolving in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill, or by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on chlorinated diphenyl oxide, look up chlorinated diphenyl oxide in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR CHLORINATED DIPHENYL OXIDE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 5 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors, acid gases, and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Chlorine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cl_2
- Synonyms: None
- Appearance and odor: Amber liquid or greenish-yellow gas with a characteristic irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine is a ceiling level of 1 part of chlorine per million parts of air (ppm) averaged over a 15-minute period (*Federal Register*, Vol. 43, No. 237, pp. 57601-03, 8 December 1978). This may also be expressed as 3 milligrams of chlorine per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 0.5 ppm (1.5 mg/m^3) measured over a 15-minute period. The NIOSH Criteria Document for Chlorine should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorine can affect the body if it is inhaled, or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Chlorine gas may cause severe irritation of the eyes and respiratory tract with tearing, runny nose, sneezing, coughing, choking, and chest pain. Severe breathing difficulties may occur which may be delayed in onset. Pneumonia may result. Severe exposures may be fatal. In high concentrations chlorine may irritate the skin and cause sensations of burning and prickling, inflammation, and blister formation. Liquid chlorine may cause eye and skin burns on contact.

2. Long-term Exposure: Repeated or prolonged exposure to chlorine may cause corrosion of the teeth and skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorine at potentially hazardous levels:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, cardiac status, and teeth should be stressed. The skin should be examined for evidence of chronic disorders. Simple tests of olfactory ability should be carried out.

—14" x 17" chest roentgenogram: Chlorine causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chlorine is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The above medical examinations are to be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Chlorine gas is a severe irritant of the eyes, mucous membranes, and skin. The odor threshold for chlorine has been reported at various concentrations and appears to be between 0.02 and 0.2 ppm for most subjects. Nasal irritation and coughing occur at about 0.5 ppm. There is evidence that olfactory fatigue develops at these low concentrations and that some tolerance is built up in

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chronic industrial exposures. An accidental exposure of humans to unmeasured but high concentrations for a brief period caused burning of the eyes with lacrimation, burning of the nose and mouth with rhinorrhea, cough, choking sensation and substernal pain. These symptoms were frequently accompanied by nausea, vomiting, headache, dizziness, and sometimes syncope. Of 33 of the victims who were hospitalized, all suffered tracheobronchitis, 23 progressed to pulmonary edema, and of those, 14 to pneumonitis. Respiratory distress and substernal pain generally subsided within the first 72 hours; cough increased in frequency and severity after 2 to 3 days and became productive of thick mucopurulent sputum; cough disappeared by the end of 14 days. Prolonged or repeated exposure to 5 ppm may cause respiratory complaints, corrosion of the teeth, and inflammation of the mucous membranes of the nose. It has been reported that chronic exposure may increase susceptibility to respiratory infections. In high concentrations, chlorine irritates the skin and causes sensations of burning and pricking, inflammation, and vesicle formation. Liquid chlorine causes eye and skin burns on contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 70.9
2. Boiling point (760 mm Hg): −34.1 C (−29.3 F)
3. Specific gravity (water = 1): 1.41 (liquid)
4. Vapor density (air = 1 at boiling point of chlorine): 2.5
5. Melting point: −101 C (−149 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.7
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Contact with combustible substances (such as gasoline and petroleum products, turpentine, alcohols, acetylene, hydrogen, ammonia, and sulfur) and finely divided metals may cause fires and explosions.
3. Hazardous decomposition products: None.
4. Special precautions: Chlorine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but is a strong oxidizer.
2. Compressed gas cylinders containing chlorine should be stored in accordance with 29 CFR 1910.101.

- **Warning properties**

1. Odor Threshold: The odor threshold for chlorine has been reported by several authors to be 0.01 ppm (Summer, May, and Stern).
2. Eye Irritation Level: Grant states that "exposure to concentrations of chlorine gas as low as 3 to 6 ppm in air causes sensation of stinging and burning of the eyes of some individuals, with associated blepharospasm, redness, and watering, but on continued exposure sensitivity may decrease and signs and symptoms diminish."

The ILO states that eye irritation may occur at 1 to 3 ppm.

3. Other Information: Patty states that "exposures to low concentrations, 10 to 20 mg/m^3 or 3 to 6 ppm, cause a stinging or burning sensation in the eyes, nose and throat, and sometimes headache due to irritation of the accessory nasal sinuses. There may be redness and watering of the eyes, sneezing, coughing, and huskiness or loss of the voice. Bleeding of the nose may occur, and sputum from the pharynx and trachea may be blood-tinged. There is little or no chest pain other than the muscular soreness associated with excessive coughing."
4. Evaluation of Warning Properties: Through its odor, chlorine can be detected below the permissible exposure limit, and through its irritant effects, chlorine can be detected within several times of the permissible exposure limit. For the purposes of this guideline, therefore, chlorine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chlorine. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorine may be used. An analytical method for chlorine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may

be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorine, and to prevent the skin from becoming frozen from contact with vessels containing liquid chlorine.
- Where there is any possibility of exposure of an employee's body to liquid chlorine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chlorine should be removed immediately and not reworn until the chlorine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid chlorine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid chlorine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chlorine should be immediately washed or showered to remove any chlorine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorine may occur and control methods which may be effective in each case:

Operation	Controls
Use as chlorinating and oxidizing agent in organic synthesis, manufacture of solvents, automotive antifreeze and antiknock compounds, plastics, resins, elastomers, pesticides, refrigerants, bleaching, and inorganic chemicals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as fluxing, purification, and extraction agent in metallurgy	Process enclosure; local exhaust ventilation
Use as bacteriostat, disinfectant, odor control, and demulsifier in treatment of water and sewage	Process enclosure; local exhaust ventilation
Use as a chlorinating agent in the rubber and coatings industry	Process enclosure; local exhaust ventilation
Use as bleaching agent, cleaning agent, and disinfectant in laundries, dishwashers, cleaning powders, cleaning dairy equipment, and bleaching cellulose	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid chlorine or high concentrations of chlorine gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid chlorine or high concentrations of chlorine gas get on the skin, immediately flush the contaminated skin with water. If liquid chlorine or high concentrations of chlorine gas penetrate through the clothing, remove the clothing and immediately flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If chlorine is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty through a reducing agent, such as sodium bisulfide and sodium bicarbonate.

- Waste disposal method:

Chlorine may be disposed of by allowing gas to disperse at a safe location.

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RESPIRATORY PROTECTION FOR CHLORINE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Gas Concentration	
25 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against chlorine.** A gas mask with a chin-style or a front- or back-mounted canister providing protection against chlorine.** Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 25 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any full-facepiece gas mask providing protection against chlorine.** Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Chlorine is a strong oxidizer and should not come in contact with oxidizable materials.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorine; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 25 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorine Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ClO_2
- Synonyms: None
- Appearance and odor: Yellow-green to orange gas or liquid with a pungent, sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine dioxide is 0.1 part of chlorine dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.3 milligram of chlorine dioxide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorine dioxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chlorine dioxide may cause irritation of the eyes, nose, throat, and lungs. It may produce coughing, wheezing, and severe breathing difficulties which may be delayed in onset.

2. Long-term Exposure: Repeated exposure to chlorine dioxide may cause chronic bronchitis.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorine dioxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system and eyes should be stressed.

—14" x 17" chest roentgenogram: Chlorine dioxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chlorine dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Chlorine dioxide gas is a severe respiratory and eye irritant. Delayed deaths occurred in animals after exposure to 150 to 200 ppm for less than 1 hour. Rats repeatedly exposed to 10 ppm died after 10 to 13 days of exposure; there was nasal and ocular discharge and dyspnea; autopsy revealed purulent bronchitis. Exposure of a worker to 19 ppm for an unspecified time period was fatal. Repeated acute exposure of workers to undetermined concentrations is stated to have caused eye and throat irritation, nasal discharge, cough, wheezing, bronchitis, and delayed onset of pulmonary edema. Repeated exposure may cause chronic bronchitis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 67.5
2. Boiling point (760 mm Hg): 11 C (52 F)
3. Specific gravity (water = 1): 1.6 (Liquid at boiling point)
4. Vapor density (air = 1 at boiling point of chlorine dioxide): 2.3
5. Melting point: −59 C (-74 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8 (commercial solutions)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 130 C (266 F) cause rapid decomposition of gas. It will detonate if heated rapidly to 100 C (212 F).
2. Incompatibilities: Contact with dust and other combustible materials such as organic matter and sulfur may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine gas) may be released when chlorine dioxide decomposes.
4. Special precautions: Chlorine dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Self-accelerating decomposition temperature: 130 C (266 F)
3. Explosive limits in air: Concentrations over 40 percent in air will sustain a decomposition wave set off by an electric spark. Gas is explosive at concentrations over 10 percent and can be ignited by almost any form of energy such as sunlight, heat, or sparks.
4. Extinguishant: None known

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for chlorine dioxide of 0.1 ppm.
2. Eye Irritation Level: Grant states that "chlorine dioxide is a reddish yellow, poisonous gas which is very irritating to the respiratory tract. Industrially, men exposed to low concentrations of the gas in air have been noted occasionally to suffer from irritation of the eyes and to see haloes about lights, but these effects have been minor compared to respiratory irritation. The corneas of workers seeing haloes have not been examined to determine whether epithelial edema is present and responsible for this symptom." The *Documentation of TLV's* notes that "Elkins stated that a concentration of chlorine dioxide (ClO_2) of 5 ppm was definitely irritating."
3. Evaluation of Warning Properties: Since the odor threshold of chlorine dioxide is at the permissible exposure limit, this substance could be treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for chlorine dioxide had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorine dioxide.
- Where there is any possibility of exposure of an employee's body to liquid chlorine dioxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chlorine dioxide and any clothing which becomes wet with liquid chlorine dioxide should be removed immediately and not reworn until the chlorine dioxide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any

possibility of liquid chlorine dioxide contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquid chlorine dioxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chlorine dioxide should be immediately washed or showered with soap or mild detergent and water to remove any chlorine dioxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorine dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Use as bleaching agent for wood pulp and paper and textiles	Process enclosure; local exhaust ventilation; personal protective equipment
Use in water treatment to remove tastes and odors by oxidation; use in bleaching fats and oils, and to improve product, and leather dressing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as bleaching and maturing agent in flour for baking; use as bleaching, cleaning, and unhairing agent in leather manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as oxidizing agent; use in control of microorganisms in fruit and vegetable processing as oxidizing agent; and as bacteria and algae control in aquariums and packaged pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid chlorine dioxide or strong concentrations of chlorine dioxide vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid chlorine dioxide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid chlorine dioxide penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorine dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid chlorine dioxide has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the chlorine dioxide. Do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorine dioxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, evacuate persons not wearing protective equipment from spill area. Allow chlorine dioxide to evaporate while providing all available ventilation.

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RESPIRATORY PROTECTION FOR CHLORINE DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
5 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) containing non-combustible sorbents and providing protection against chlorine dioxide. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against chlorine dioxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-combustible sorbents and providing protection against chlorine dioxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Chlorine Trifluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ClF_3
- Synonyms: None
- Appearance and odor: Greenish-yellow, almost colorless liquid or gas with a sweet, but irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine trifluoride is a ceiling level of 0.1 part of chlorine trifluoride per million parts of air (ppm). This may also be expressed as 0.4 milligram of chlorine trifluoride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorine trifluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Effects on humans from exposure to chlorine trifluoride have not been reported. Animal experiments have shown that exposure to this chemical can cause severe irritation of the eyes and respiratory tract. Severe breathing difficulties have occurred. These difficulties may sometimes be delayed in onset. Severe burns of the eyes and skin have been produced in animals from contact with this chemical.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine trifluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorine trifluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin and eyes should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Chlorine trifluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chlorine trifluoride is a severe pulmonary irritant in animals. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Chlorine trifluoride gas is an extremely severe irritant of the eyes, respiratory tract, and skin. The injury caused by chlorine trifluoride can be extremely severe and, in part, attributed to its hydrolysis products including chlorine, hydrogen fluoride, and chlorine dioxide. Exposure of rats to 800 ppm for 15 minutes was fatal, but nearly all survived when exposed for 13 minutes. There was severe inflammation of all exposed mucosal surfaces, resulting in lacrimation, corneal ulceration, and burning of exposed areas of skin. In another study, exposure of rats to 480 ppm for 40 minutes or to 96 ppm

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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for 3.7 hours was fatal; in the latter group, there were pulmonary edema and marked irritation of the bronchial mucosa. Effects in humans have not been reported, but exposure may cause some effects; inhalation may be expected to cause pulmonary edema, and contact with eyes or skin may cause severe burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 92.5
2. Boiling point (760 mm Hg): 11.8 C (53 F)
3. Specific gravity (water = 1): 1.88 (liquid)
4. Vapor density (air = 1 at boiling point of chlorine trifluoride): 3.14
5. Melting point: −76.3 C (-105 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Violent reaction to form chlorine gas and hydrofluoric acid
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Chlorine trifluoride decomposes above 220 C (428 F) and may explode container.
2. Incompatibilities: Chlorine trifluoride will cause most combustible materials to ignite spontaneously. The exceptions are dry, highly fluorinated polymers such as "Teflon" and "Kel-F," the metals used in storage containers (monel, copper, and stainless steel) or gaskets (teflon), nitrogen gas or air, and the inert gases (neon, etc.). Chlorine trifluoride reacts violently with water, sand, silicon-containing compounds, glass, and asbestos.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen fluoride) may be released when chlorine trifluoride decomposes.
4. Special precautions: Chlorine trifluoride will attack all forms of plastics, rubber, and resins, except the higly fluorinated polymers "Teflon" and Kel-F."

- **Flammability**

1. Not combustible by itself, but is very reactive and may cause fire on contact with organic matter.

- **Warning properties**

Odor Threshold: Deichmann and Gerarde note that chlorine trifluoride has a "somewhat sweet odor." No quantitative information is available, however, concerning the odor threshold.

2. Irritation Level: Grant states that "chlorine trifluoride is an extremely reactive, corrosive and irritating gas which experimentally has been observed to cause a severe reaction in the lungs and in all exposed mucous membranes. It is highly irritating to the skin and eyes, and has caused severe corneal ulcers in dogs."

3. Evaluation of Warning Properties: Since no quantitative data are available relating warning properties to air concentrations of chlorine trifluoride, this gas is treated as a material with poor warning properties. In addition, since chlorine trifluoride is a powerful oxidizer, it should not be allowed to contact combustible materials.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chlorine trifluoride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

At the time of publication of this guideline, no measurement method for chlorine trifluoride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorine trifluoride.
- Where there is any possibility of exposure of an employee's body to liquid chlorine trifluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes contaminated with chlorine trifluoride should be removed immediately and

not reworn until the chlorine trifluoride is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid chlorine trifluoride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid chlorine trifluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chlorine trifluoride should be immediately washed or showered to remove any chlorine trifluoride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorine trifluoride may occur and control methods which may be effective in each case:

Operation	Controls
use as a fluorinating agent in organic and inorganic chemical synthesis; use in the separation of uranium isomers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a cutting agent for well castings in oil well drilling	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a rocket fuel oxidizer as an igniter and propellant in liquid propellant engines; use as an incendiary	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor get on the skin, immediately flush the contaminated skin with large quantities of water. If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor penetrate through the clothing, remove the clothing immediately and flush the skin with large amounts of water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of chlorine trifluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid chlorine trifluoride has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the chlorine trifluoride. Do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorine trifluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in the liquid form, evacuate persons not wearing protective equipment from spill area. Allow chlorine trifluoride to evaporate while providing all available ventilation.

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RESPIRATORY PROTECTION FOR CHLORINE TRIFLUORIDE

Condition	**Minimum Respiratory Protection* Required Above 0.1 ppm**
Gas Concentration	
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A gas mask containing non-combustible sorbents and providing protection against chlorine trifluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorine trifluoride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chloroacetaldehyde

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $ClCH_2CHO$
- Synonyms: 2-Chloroethanal; chloroacetaldehyde (40% aqueous)
- Appearance and odor: Colorless liquid with a very sharp, irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chloroacetaldehyde is a ceiling level of 1 part of chloroacetaldehyde per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3 milligrams of chloroacetaldehyde per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloroacetaldehyde can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

Chloroacetaldehyde causes skin burns, irritation of the throat, nose, and lungs, and serious irritation of the eyes.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chloroacetaldehyde.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chloroacetaldehyde at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from chloroacetaldehyde exposure.

—Eye disease: Chloroacetaldehyde is a potent eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—Skin disease: Chloroacetaldehyde is a skin irritant and possibly a skin sensitizer. Those with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chloroacetaldehyde might cause exacerbation of symptoms due to its irritant and potentially sensitizing properties.

—Kidney disease: Although chloroacetaldehyde is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although chloroacetaldehyde is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Overexposure to chloroacetaldehyde produces corrosive destruction and degradation of lipids and membrane structures, causing intense irritation and edema of the eyes, mucous membranes, respiratory tract, and skin. Prolonged exposure to the liquid causes tissue destruction, chemical burns, and residual scarring. Some permanent damage to the eye may occur. Chloroacetaldehyde and its metabolite, chloroacetic acid, are

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excreted by the kidneys. The possibility of skin and respiratory sensitization should be considered.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 78.5
2. Boiling point (760 mm Hg): 85 C (185 F)
3. Specific gravity (water = 1): 1.19 for 40% aqueous solution
4. Vapor density (air = 1 at boiling point of chloroacetaldehyde): 2.7 for 40% aqueous solution
5. Melting point: −16.3 C (3 F) for 40% aqueous solution
6. Vapor pressure at 45 C (113 F): 100 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with oxidizing materials and acids may cause fires or explosions. The compound reacts with water to form a hydrate with the evolution of some heat.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving chloroacetaldehyde.
4. Special precautions: Chloroacetaldehyde forms a water-insoluble polymer in storage, especially in the presence of small amounts of acid.

- **Flammability**

1. Flash point: 88 C (190 F)(closed cup) for 40% aqueous solution
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam

- **Warning properties**

1. Odor Threshold: By analogy to crotonaldehyde and acetaldehyde, both of which the *Handbook of Organic Industrial Solvents* states have odor thresholds less than 1 ppm, the odor threshold of chloroacetaldehyde is assumed to be less than 1 ppm.
2. Irritation Levels: The *Documentation of TLV's* states that "chloroacetaldehyde presents a serious hazard from inhalation of its vapor, which is irritating to the eyes, nose, and throat . . . . This aldehyde is somewhat more irritating than formaldehyde."

According to Grant, formaldehyde causes "definite irritation of the eyes and lacrimation . . . at a concentration of 20 ppm in air. Even at concentrations from 0.5 to 0.005 ppm a sensation of eye irritation is detectable, and it (formaldehyde) can be sensed as low as 0.01 ppm by some people."

The *Documentation of TLV's*, in addition, states that a "threshold limit of 1 ppm (chloroacetaldehyde) is recommended to prevent irritative effects. Analogy with other aldehydes and practical experience suggest that the TLV will not prevent all complaints of irritation, and it should be used only with caution in continuous, repeated exposure situations."

3. Evaluation of Warning Properties: By analogy to other aldehydes, it is assumed that chloroacetaldehyde can be detected at the permissible exposure through its odor and irritant effects. For the purposes of this guideline, therefore, chloroacetaldehyde is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chloroacetaldehyde. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

An analytical method for chloroacetaldehyde is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent any possibility of skin contact with chloroacetaldehyde at or above a concentration of 0.1%.

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing chloroacetaldehyde below a concentration of 0.1%.
- Clothing contaminated with chloroacetaldehyde should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chloroacetaldehyde from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chloroacetaldehyde, the person performing the operation should be informed of chloroacetaldehyde's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solutions containing in excess of 0.1% chloroacetaldehyde, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chloroacetaldehyde should be removed immediately and not reworn until the chloroacetaldehyde is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid chloroacetaldehyde contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid chloroacetaldehyde, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chloroacetaldehyde should be immediately washed or showered to remove any chloroacetaldehyde.
- Employees who handle liquid chloroacetaldehyde should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chloroacetaldehyde may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture of 2-aminothiazole	Process enclosure; general dilution ventilation; personal protective equipment (with barrier creams)
Liberation during use in diethylacetal in acid media during chemical synthesis, such as p-aminothiazole	Process enclosure; general dilution ventilation; personal protective equipment
Use during control of algae, bacteria, and fungi in water	General dilution ventilation; personal protective equipment (with barrier creams)
Use as a spinning solution of poly B-alanine	General dilution ventilation; personal protective equipment (with barrier creams)
Liberation from intermediate steps in organic synthesis	Local exhaust ventilation
Use during debarking operations	Local exhaust ventilation; personal protective equipment
Use of diethylacetal in an acid media during chemical synthesis such as p-aminothiazole	Process enclosure; general dilution ventilation; personal protective equipment (with barrier creams)

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chloroacetaldehyde gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible.

- **Skin Exposure**

If chloroacetaldehyde gets on the skin, immediately flush the contaminated skin with water. If chloroacetaldehyde soaks through the clothing, remove the clothing immediately and flush the skin with water. When there are chemical burns or evidence of skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of chloroacetaldehyde, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chloroacetaldehyde has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chloroacetaldehyde is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Chloroacetaldehyde may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR CHLOROACETALDEHYDE

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
50 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 250 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for alpha-Chloroacetophenone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5COCH_2Cl$
- Synonyms: Phenyacyl chloride; omega=chloroacetophenone; chloroacetophenone; chloromethyl phenyl ketone; phenyl chloromethyl ketone; "tear gas"; CN
- Appearance and odor: Colorless to gray solid with a sharp, irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for alpha-chloroacetophenone is 0.05 part of alpha-chloroacetophenone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.3 milligram of alpha-chloroacetophenone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

alpha-Chloroacetophenone can cause irritation of the eyes and skin upon contact and irritation of the lungs if it is inhaled. It can also cause difficulty if it is swallowed.

- **Effects of overexposure**

alpha-Chloroacetophenone vapors may cause a tingling or runny nose, burning and/or pain of the eyes, blurred vision, and tears. Burning in the chest, difficult breathing, and nausea may occur. Skin irritation, rash, or burns may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to alpha-chloroacetophenone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to alpha-chloroacetophenone at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from alpha-chloroacetophenone exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of alpha-chloroacetophenone might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Skin disease: alpha-Chloroacetophenone is irritating to the skin, especially if moist. Persons with pre-existing skin diseases may be more susceptible to the effects of alpha-chloroacetophenone.

—Eye disease: alpha-Chloroacetophenone is a potent lacrimator and eye irritant and may cause corneal damage. Persons with pre-existing eye diseases may be at increased risk from exposure.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

alpha-Chloroacetophenone is a highly irritating substance. Exposure to low concentrations produces lacrimation and irritation of the eyes and upper respiratory tract. Exposure to high concentrations produces marked conjunctivitis and may cause corneal damage. Pulmonary edema may occur, often delayed for some 12 hours after exposure. No chronic effects are reported.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 155
2. Boiling point (760 mm Hg): 247 C (477 F)
3. Specific gravity (water = 1): 1.32
4. Vapor density (air = 1 at boiling point of alpha-chloroacetophenone): 5.2
5. Melting point: 59 C (138 F)
6. Vapor pressure at 20 C (68 F): 0.012 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Very much less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Water or steam
3. Hazardous decomposition products: Toxic and corrosive vapors are produced when combined with steam or water.
4. Special precautions: None

- **Flammability**

1. Flash point: 118 C (244 F)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Carbon dioxide or dry chemical

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, the odor threshold is 0.1 mg/m^3.
2. Irritation Levels: According to the *Documentation of TLV's*, "irritation thresholds range from 0.15 to 0.4 mg/m^3, lacrimation thresholds from 0.3 to 0.4 mg/m^3. . . ."
3. Evaluation of Warning Properties: Through its odor and irritant effects, alpha-chloroacetophenone can be detected below the permissible exposure limit; therefore, it is considered to have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for alpha-chloroacetophenone is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid alpha-chloroacetophenone or liquids containing alpha-chloroacetophenone.
- If employees' clothing may have become contaminated with solid alpha-chloroacetophenone, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with alpha-chloroacetophenone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of alpha-chloroacetophenone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the alpha-chloroacetophenone, the person performing the operation should be informed of alpha-chloroacetophenone's hazardous properties.
- Non-impervious clothing which becomes contaminated with alpha-chloroacetophenone should be removed immediately and not reworn until the alpha-chloroacetophenone is removed from the clothing.
- Where there is any possibility that employees' eyes may be exposed to alpha-chloroacetophenone, an eye-wash fountain should be provided within the immediate work area for emergency use.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid alpha-chloroacetophenone or liquids containing alpha-chloroacetophenone contacting the eyes.

SANITATION

- Skin that becomes contaminated with alpha-chloroacetophenone should be immediately washed or showered with soap or mild detergent and water to remove any alpha-chloroacetophenone.
- Eating and smoking should not be permitted in areas where solid alpha-chloroacetophenone is handled, processed, or stored.
- Employees who handle solid alpha-chloroacetophenone or liquids containing alpha-chloroacetophenone should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to alpha-chloroacetophenone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during loading of solutions for aerosols for law enforcement and civilian protective devices	General dilution ventilation; respiratory protective equipment
Liberation during manufacture	Process enclosure; general dilution ventilation
Liberation during denaturing of industrial alcohol	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If alpha-chloroacetophenone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If alpha-chloroacetophenone gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If alpha-chloroacetophenone soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. When there are chemical burns or evidence of skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of alpha-chloroacetophenone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When alpha-chloroacetophenone has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If alpha-chloroacetophenone is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

alpha-Chloroacetophenone may be disposed of:

1. By making packages of alpha-chloroacetophenone in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving alpha-chloroacetophenone in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR ALPHA-CHLOROACETOPHENONE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Particulate and Vapor Concentration	
15 mg/m^3 (2.5 ppm) or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s) and high efficiency particulate filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister with a high efficiency particulate filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 (16 ppm) or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 mg/m^3 (16 ppm) or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROACETYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about chloroacetyl chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_2H_2Cl_2O$

- **Structure**

  $ClCH_2COCl$

- **Synonyms**

  Chloroacetic acid chloride; chloroacetic chloride; monochloroacetyl chloride; chloracetyl chloride

- Identifiers

  1. CAS No.: 79-04-9
  2. RTECS No.: AO6475000
  3. DOT UN: 1752 59
  4. DOT label: Corrosive

- **Appearance and odor**

  Chloroacetyl chloride is a colorless to slightly yellow liquid with a strong, pungent odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.94
  2. Boiling point (760 mm Hg): 105° to 110°C (221° to 230°F)
  3. Specific gravity (water = 1): 1.42 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chloroacetyl chloride): Data not available
  5. Melting point (at 760 mm Hg): 106°C (222.8°F)
  6. Freezing point: -22.5°C (-8.5°F)
  7. Vapor pressure at 21°C (69.8°F): 20 mm Hg
  8. Solubility: Insoluble in water; soluble in ether and acetone
  9. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and water
  2. Incompatibilities: Contact of chloroacetyl chloride

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with water causes decomposition and the release of hydrogen chloride gas and chloroacetic acid; avoid contact with alcohols, amines, and alkalis.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and chlorine) may be released in a fire involving chloroacetyl chloride.
4. Special precautions: Keep chloroacetyl chloride away from moisture or water.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloroacetyl chloride; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire. Do not use water.

Fires involving chloroacetyl chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloracetyl chloride should be moved from the fire area if it is possible to do so safely. If this is not possible, cool fire-exposed containers from the sides with water until well after the fire is out. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloroacetyl chloride. Chemical protective clothing that is specifically recommended for chloroacetyl chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloroacetyl chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloroacetyl chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.2 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloroacetyl chloride a threshold limit value (TLV) of 0.05 ppm (0.23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm (0.69 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 minutes. The ACGIH has also assigned a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of skin and respiratory irritation associated with choloracetyl chloride exposure. The ACGIH limits are based on the risk of eye, skin, and respiratory irritation and systemic effects associated with exposure to chloroacetyl chloride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloroacetyl chloride can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloroacetyl chloride is highly corrosive to tissues; in animals it affects the lungs, eyes, and skin. In rabbits the dermal LD_{50} is 178 mg/kg and the dermal LD_{LO} ranges from 316 to 501 mg/kg [AIHA 1987; NIOSH 1989; ACGIH 1991]. The LC_{50} in the rat is 1,000 ppm for a 4-hr exposure [NIOSH 1989]. A 5 to 10 min exposure to a

concentration of 4 ppm caused respiratory difficulty in rats, but no effect was observed from the inhalation of a 2.5-ppm chloroacetyl chloride concentration for 7 hr [NLM 1992; AIHA 1987]. A 30-day inhalation study with rats, mice, and hamsters showed that these animals develop eye and respiratory irritation at an airborne concentration of 2.5 ppm [NLM 1992]. The oral LD_{50} in the rat is 120 mg/kg; cough and dermatitis were noted before death [NIOSH 1989].

2. *Effects on Humans:* In humans, chloroacetyl chloride is corrosive to the skin and eyes and affects the respiratory system [Sittig 1985]. The effects of acute workplace exposure include mild to moderate skin irritation and burns, lacrimation, mild eye burns, mild to moderate respiratory effects with cough, dyspnea, cyanosis, and mild gastrointestinal effects [ACGIH 1991; AIHA 1987]. Respiratory effects include coughing, difficult breathing, and oxygen insufficiency [ACGIH 1991a]. Workers exposed to peak chloroacetyl chloride concentrations of 140 ppb developed eye irritation and reported experiencing minimal respiratory irritation [NLM 1992]. In an industrial accident, a worker was drenched by a mixture containing chloroacetyl chloride, xylidine, benzene, and sodium carbonate. Although immediately put under a shower, he suffered extensive first- and second-degree burns, developed pulmonary edema, and had three episodes of cardiac arrest during emergency treatment. He went into a coma that lasted several weeks; the ultimate outcome of this case is not reported [ACGIH 1991; NLM 1992]. Workers involved in the rescue of this employee suffered blisters on their hands and complained of tightness of the chest and slight nausea for as long as 2 days after the incident [NLM 1992]. Most of the acute effects experienced by this worker are believed to have been caused by the chloroacetyl chloride.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation overexposure to chloroacetyl chloride include pain, redness, and tearing of the eyes, sore throat, pain in the chest, fluid in the lungs, and difficult breathing. Contact with the liquid can cause severe skin or eye burns.

2. *Chronic exposure:* The signs and symptoms of continued low-level exposure to chloroacetyl chloride may include a burning sensation in the upper respiratory tract, wheezing, laryngitis, and shortness of breath.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of chloroacetyl chloride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloroacetyl chloride or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloroacetyl chloride and may result in worker exposures to this substance:

—Manufacture of herbicides (such as alachlor, allidochlor, butachlor, and others) and tear gas

—Use as an intermediate in the manufacture of chloroacetophenone and other chemicals

—Manufacture of pharmaceuticals, such as chlordiazepoxide hydrochloride, diazepam, lidocaine, and mianserin

The following methods are effective in controlling worker exposures to chloroacetyl chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Personal protective equipment and local ventilation are a necessity at chloroacetyl chloride transfer points where leakage can be expected.

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chloroacetyl chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloroacetyl chloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloroacetyl chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloroacetyl chloride on the respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloroacetyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloroacetyl chloride is determined by using a XAD-2 tube coated with 1- (2-pyridyl)piperazine. Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 10 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If chloroacetyl chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with chloroacetyl chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chloroacetyl chloride, particularly its potential to cause eye and skin burns.

A worker who handles choloroacetyl chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloroacetyl chloride or a solution containing chloroacetyl chloride is handled, processed, or stored.

STORAGE

Chloroacetyl chloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloroacetyl chloride should be protected from physical damage and should be stored separately from water, steam, surface moisture, oxidizing agents, strong bases, alcohols, heat, sparks, and open flame. Because containers that formerly contained chloroacetyl chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloroacetyl chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the chloroacetyl chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloroacetyl chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloroacetyl chloride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloroacetyl chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloroacetyl chloride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloroacetyl chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloroacetyl chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloroacetyl chloride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloroacetyl chloride.

If chloroacetyl chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloroacetyl chloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloroacetyl chloride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROBENZENE

INTRODUCTION

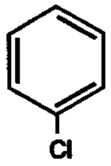
This guideline summarizes pertinent information about chlorobenzene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_6H_5Cl

- **Structure**



- **Synonyms**

Monochlorobenzene, MCB, phenyl chloride, chlorobenzol, benzene chloride

- **Identifiers**

1. CAS No.: 108-90-7
2. RTECS No.: CZ0175000
3. DOT UN: 1134 27
4. DOT label: Flammable liquid

- **Appearance and odor**

Chlorobenzene is a colorless to yellowish liquid with a mild, aromatic, almond-like odor. The odor threshold of chlorobenzene is 0.21 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 112.6
2. Boiling point (760 mm Hg): 131° to 132°C (267.8° to 270°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of chlorobenzene): 3.9
5. Melting point: -45°C (-49°F)

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 8.8 mm Hg

7. Solubility: Insoluble in water; soluble in alcohol, benzene, chloroform, and ether

8. Evaporation rate (ether = 1): 8.2

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of chlorobenzene with strong oxidizers, dimethyl sulfoxide, powdered sodium, phosphorus trichloride and sodium, or silver perchlorate causes fire, explosion, or a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chlorobenzene.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to chlorobenzene.

1. Flash point: 27.8°C (82°F)

2. Autoignition temperature: 593°C (1,099°F)

3. Flammable limits in air (% by volume): Lower, 1.3; upper, 9.6

4. Extinguishant: Use carbon dioxide, dry chemical, water spray, or standard foam to fight fires involving chlorobenzene.

Fires involving chlorobenzene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of chlorobenzene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorobenzene. Structural firefighters' protective clothing may provide limited protection against fires involving chlorobenzene.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chlorobenzene is 75 ppm (350 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for chlorobenzene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorobenzene a threshold limit value (TLV) of 10 ppm (46 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of liver and other effects associated with exposure to chlorobenzene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorobenzene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

  1. *Effects on Animals:* Exposure to chlorobenzene causes irritation, narcosis, and liver and kidney damage. In contact with the eyes of rabbits or skin of guinea pigs, chlorobenzene caused a moderate degree of irritation [ACGIH 1991]. Rats, rabbits, and guinea pigs exposed to chlorobenzene at a concentration of 1,000 ppm for 7 hr/day, 5 days/week for 44 days showed signs of lung, liver, and kidney damage; however, exposure to a 475-ppm concentration on the same regimen caused only slight liver damage in one species [Hathaway et al. 1991; ACGIH 1991]. Cats exposed to an 8,000-ppm concentration of chlorobenzene for 30 min showed signs of severe narcosis and died 2 hr after cessation of exposure; however, cats survived exposure to a 660-ppm concentration for 1 hr [Hathaway et al. 1991]. Acutely poisoned animals showed signs of eye and nose irritation and narcosis [Hathaway et al. 1991]. The oral LD_{50} in rats is 2,290 mg/kg, and the lowest lethal concentration in mice is 15 g/m^3 [NIOSH 1993]. In gavage studies of rats and mice administered chlorobenzene 5 days/week for 91 days, dose-dependent necrosis of the liver, degeneration or focal necrosis of the proximal tubules of the kidney, and myeloid or lymphoid depletion of the spleen, bone marrow, and thymus were seen at doses of 250 mg/kg/day or greater in both sexes [Hathaway et al. 1991]. In 2-year gavage studies of male and female rats and mice, male rats administered chlorobenzene doses of 120 mg/kg had a slight but statistically significant increase in neoplastic nodules of the liver. No increase in the incidence of liver tumors was seen in the mice or the female rats [Hathaway et al. 1991].

  2. *Effects on Humans:* Exposure to chlorobenzene at a concentration of 200 ppm causes eye and nose irritation, and exposure to higher concentrations causes central nervous system depression. In contact with the skin for brief exposures, liquid chlorobenzene causes only mild irritation; however, prolonged or repeated contact can lead to burns of the skin [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

  1. *Acute exposure:* Acute exposure to chlorobenzene may cause redness and inflammation of the eyes and eyelids, runny nose, sore throat, redness and irritation of the skin, headache, dizziness, drowsiness, incoherence, ataxia, loss of consciousness, twitching of the extremities, deep and rapid respiration, and irregular heartbeat. Respiratory arrest may follow.

  2. *Chronic exposure:* Long-term exposure to chlorobenzene may cause chronic central nervous system depression: headache, dizziness, and somnolence. Based on effects seen in animals, chronic exposure may cause elevated liver enzymes, enlarged and tender liver, and blood, pus, or protein in the urine. Prolonged or repeated skin contact may cause skin burns.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of chlorobenzene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chlorobenzene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorobenzene and may result in worker exposures to this substance:

—Use as a solvent for paints, adhesives, polishes, waxes, and natural rubber, and as a solvent carrier for methylene diisocyanate

—Use as a dry-cleaning agent

—Manufacture of phenol, o- and p-chloronitrobenzene, aniline, DDT, and pharmaceuticals

The following methods are effective in controlling worker exposures to chlorobenzene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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Before a worker is placed in a job with a potential for exposure to chlorobenzene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, central nervous system, liver, eyes, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorobenzene at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or central nervous system, liver, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorobenzene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorobenzene on the respiratory or central nervous system, liver, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although chlorobenzene or its metabolites can be detected in the blood or adipose tissue of exposed individuals, no biological monitoring test acceptable for routine use has yet been developed for chlorobenzene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorobenzene is determined by using a coconut shell solid sorbent tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 40 liters is collected. The samples are then desorbed with carbon disulfide to extract the chlorobenzene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg/sample. This method is described in NIOSH Method No. 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If chlorobenzene contacts the skin, workers should flush the affected areas immediately with plenty of water, followed by washing with soap and water.

Clothing contaminated with chlorobenzene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chlorobenzene, particularly its potential to be irritating to the eyes and skin.

A worker who handles chlorobenzene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorobenzene or a solution containing chlorobenzene is handled, processed, or stored.

STORAGE

Chlorobenzene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of chlorobenzene should be protected from physical damage and should be stored separately from oxidizers, dimethyl sulfoxide, silver perchlorate, other incompatible chemicals, heat, sparks, and open flame. Only nonsparking tools may be used to handle chlorobenzene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained chlorobenzene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorobenzene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the chlorobenzene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chlorobenzene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for chlorobenzene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more of chlorobenzene per calendar year or otherwise use 10,000 lb or more of chlorobenzene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorobenzene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Chlorobenzene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U037. It is approved for land disposal as long as the concentration of chlorobenzene in the waste or treatment residual does not exceed 5.7 mg/kg. Chlorobenzene also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorobenzene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with chlorobenzene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material have demonstrated greater than 8 hr of resistance to breakthrough under continuous contact: Viton, Barricade, and Responder. Polyvinyl-alcohol and Teflon have shown resistance to breakthrough between 4 and 8 hr.

If chlorobenzene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chlorobenzene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chlorobenzene. Contact lenses should not be worn if the potential exists for chlorobenzene exposure.

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NIOSH [1984]. Chlorobenzene: Method 1003. In: Eller PM, ed. NIOSH manual of analytical methods. 3rd rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

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NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROBENZYLIDENE MALONONITRILE

INTRODUCTION

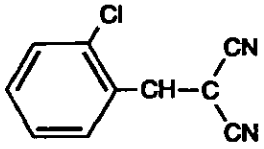
This guideline summarizes pertinent information about o-chlorobenzylidene malononitrile for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_5ClN_2$

- **Structure**



- **Synonyms**

CS; OCBM; (o-chlorobenzal)malononitrile; beta,beta-dicyano-o-chlorostyrene

- **Identifiers**

1. CAS No.: 2698-41-1
2. RTECS No.: OO3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

o-Chlorobenzylidene malononitrile is a white, crystalline solid with a pepper-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 188.6
2. Boiling point (760 mm Hg): 310° to 315°C (590° to 599°F)
3. Specific gravity (water = 1): Greater than 1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-chlorobenzylidene malononitrile): 6.5
5. Melting point: 95° to 96°C (203° to 205°F)
6. Vapor pressure at 20°C (68°F): 0.000034 mm Hg
7. Solubility: Insoluble in water; soluble in acetone, benzene, ethyl acetate, dioxane, and methylene chloride.
8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of o-chlorobenzylidene malononitrile with strong oxidizers causes a violent reaction.

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine, cyanide, and nitrogen oxides) may be released in a fire involving o-chlorobenzylidene malononitrile.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to o-chlorobenzylidene malononitrile.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: No information is available on the appropriate extinguishant to use for a fire involving o-chlorobenzylidene malononitrile.

Fires involving o-chlorobenzylidene malononitrile should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorobenzylidene malononitrile.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for o-chlorobenzylidene malononitrile is 0.05 ppm parts of air (0.4 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.4 mg/m^3) as a ceiling limit. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned a ceiling limit value of 0.05 ppm (0.39 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH has also assigned a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The OSHA, NIOSH, and ACGIH limits are based on the risk of eye and respiratory tract irritation associated with exposure to o-chlorobenzylidene malononitrile [54 Fed. Reg. 2457; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorobenzylidene malononitrile can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* o-Chlorobenzylidene malononitrile is a severe lacrimator and upper respiratory tract irritant. Human eyes are more sensitive to o-chlorobenzylidene malononitrile-induced irritation than rabbit, rat, or guinea pig eyes; however, even in extreme exposures, eye injuries are superficial and reversible [Grant 1986]. The lowest lethal concentration in rats is 1,806 mg/m^3 for 45 min [NIOSH 1993]. Rats exposed to a 1800-mg/m^3 concentration of this substance for 10 min survived, but a 60-min exposure to 2,700 mg/m^3 killed all of the animals [Hathaway et al. 1991]. The most recent oral LD$_{50}$s reported for rats are 1,366 mg/kg (male) and 1,284 mg/kg (female) [ACGIH 1991]. Earlier studies in rats reported oral LD$_{50}$s ranging from 178 to 717 mg/kg [NIOSH 1993]. This substance causes systemic cyanide poisoning when animals are exposed to high doses; the mechanism of action appears to be the release of hydrocyanic acid from one or both nitriles of the malononitrile [Gosselin et al. 1984]. Mice that were injected intraperitoneally or intravenously with o-chlorobenzylidene malononitrile or were exposed

to a concentration of 20,000 mg/m^3/min of the aerosol had cyanide in their blood and urine [ACGIH 1991].

2. *Effects on Humans:* o-Chlorobenzylidene malononitrile (OCBM) is a potent lacrimator and sternutator, and a peripheral sensory irritant in humans. This substance is the active ingredient in tear gas; exposure causes an immediate, disabling irritation of the eyes and respiratory tract in humans, but no OCBM-related deaths have been reported [Grant 1986]. Exposure to an OCBM concentration of 1.5 mg/m^3 for 90 min resulted in headaches in three of four men exposed and caused nose and eye irritation in one man [ACGIH 1991; Hathaway et al. 1991]. Contact of OCBM with the skin resulted in a burning sensation that was greatly aggravated by moisture, erythema, and vesiculation resembling second degree burns were produced [Hathaway et al. 1991]. Workers handling OCBM have developed skin sensitization; the resulting dermatitis involves the arms and neck [ACGIH 1991]. Concentrations of 4.3 to 6.7 mg/m^3 could barely be tolerated when this concentration was reached gradually over a 30-min period; subjects reported conjunctivitis, involuntary closing of the eyes, burning in the throat, cough, and chest constriction [Hathaway et al. 1991]. Concentrations greater than 10 mg/m^3 are extremely irritating and have been found to be intolerable for more than 30 seconds under test conditions; the eye irritation disappeared within an hour after cessation of exposure, and respiratory effects disappeared within a few minutes [Grant 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to o-chlorobenzylidene malononitrile may cause pain and burning of the eyes, excessive tearing, conjunctivitis, involuntary closing of the eyes, excessive salivation, nausea, vomiting, nose and throat irritation, cough, chest constriction, dizziness, headache, and redness and burning of the skin with blister formation.

2. *Chronic exposure:* Chronic exposure to o-chlorobenzylidene malononitrile may cause dermatitis of the face and arms.

- **Emergency procedures:**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water

3. *Inhalation exposure:* Move victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorobenzylidene malononitrile or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorobenzylidene malononitrile and may result in worker exposures to this substance:

—Manufacturing and formulation of o-chlorobenzylidene malononitrile for use as a riot control agent

The following methods are effective in controlling worker exposures to o-chlorobenzylidene malononitrile, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to o-chlorobenzylidene malononitrile, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorobenzylidene malononitrile at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorobenzylidene malononitrile exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorobenzylidene malononitrile on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. o-Chlorobenzylidene malononitrile can be detected in the blood of exposed individuals; however, blood concentrations of this substance do not correlate well with airborne concentrations. Therefore, no biological monitoring test acceptable for routine use has yet been developed for o-chlorobenzylidene malononitrile.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorobenzylidene malononitrile is determined by using a polytetrafluoroethylene (FA) 1-micron filter in series with a Tenax GC tube (70/35-mg sections, 35/60 mesh). Samples are collected at a maximum flow rate of 1.5 liter/min until a maximum air volume of 90 liters is collected. The samples are desorbed with 20% methylene chloride in hexane. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is approximately 0.3 µg/sample. This method is described in NIOSH Method P&CAM 304 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If o-chlorobenzylidene malononitrile contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with o-chlorobenzylidene malononitrile should be removed immediately; provisions should be made for safely removing this chemical from these articles.

A worker who handles o-chlorobenzylidene malononitrile should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where o-chlorobenzylidene malononitrile is handled, processed, or stored.

STORAGE

o-Chlorobenzylidene malononitrile should be stored in a cool, dry, well-ventilated area or in a refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorobenzylidene malononitrile should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained o-chlorobenzylidene malononitrile may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorobenzylidene malononitrile, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

5. For large spills, build dikes far ahead of the spill to contain the o-chlorobenzylidene malononitrile for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorobenzylidene malononitrile is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-chlorobenzylidene malononitrile; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorobenzylidene malononitrile emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorobenzylidene malononitrile is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorobenzylidene malononitrile exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergency situations. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with o-chlorobenzylidene malononitrile. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorobenzylidene malononitrile permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorobenzylidene malononitrile.

If o-chlorobenzylidene malononitrile is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorobenzylidene malononitrile might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorobenzylidene malononitrile. Contact lenses should not be worn if the potential exists for o-chlorobenzylidene malononitrile exposure.

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Occupational Health Guideline for Chlorobromomethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2BrCl
- Synonyms: Bromochloromethane; methylene chlorobromide; CB; CBM; Halon 1011
- Appearance and odor: Colorless to pale yellow liquid with a characteristic, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorobromomethane is 200 parts of chlorobromomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1050 milligrams of chlorobromomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorobromomethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chlorobromomethane may cause irritation of the eyes and throat. It may also cause mental confusion, dizziness, and unconsciousness.

2. Long-term Exposure: Prolonged or repeated skin exposure may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorobromomethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorobromomethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from chlorobromomethane exposure.

—Skin disease: Chlorobromomethane can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although chlorobromomethane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although chlorobromomethane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chlorobromomethane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Chlorobromomethane vapor is a narcotic and a respiratory irritant. Concentrations near 30,000 ppm were fatal to mice and rats within 15 minutes; this level of exposure produced pulmonary edema and, in delayed deaths, interstitial pneumonitis. The LC50 for mice on 8-hour exposure was 3000 ppm; the predominant observation was narcosis. No toxic effects were observed in several species after repeated inhalation exposures at 1000 ppm for 14 weeks. The substance is a mild skin

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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irritant in animals. A reported exposure of three firefighters to unknown but very high vapor concentrations was characterized by disorientation, headache, nausea, and irritation of the eyes and throat; two of the three became comatose; of these, one had convulsive seizures and the other had respiratory arrest, from which he was resuscitated. Recovery was slow but complete. Some effects may have been due to the inhalation of thermal decomposition products.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 129.4
  2. Boiling point (760 mm Hg): 67.8 C (154 F)
  3. Specific gravity (water = 1): 1.93
  4. Vapor density (air = 1 at boiling point of chlorobromomethane): 4.5
  5. Melting point: −88 C (−126 F)
  6. Vapor pressure at 20 C (68 F): 117 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.9
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Chlorobromomethane reacts with chemically active metals such as calcium, powdered aluminum, zinc, and magnesium.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, carbon monoxide, and hydrogen bromide) may be released when chlorobromomethane decomposes.
  4. Special precautions: Liquid chlorobromomethane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

Patty states that "chlorobromomethane has a distinctive odor at 400 ppm. It is a good warning at well before acutely hazardous concentration. The odor is distinctive at the acceptable concentration and so gives some warning, but it is not disagreeable enough to drive anyone from the area, and workmen may well tolerate a level well above the acceptable level for chronic exposure."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorobromomethane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorobromomethane may be used. An analytical method for chlorobromomethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid chlorobromomethane.
- Non-impervious clothing which becomes wet with liquid chlorobromomethane should be removed promptly and not reworn until the chlorobromomethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorobromomethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid chlorobromomethane should be promptly washed or showered with soap or mild detergent and water to remove any chlorobromomethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorobromomethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a fire extinguishing fluid in vaporizing fire extinguishers; use in manufacture of vaporizing liquid fire extinguishers	Material substitution
Use in mineral and salt separations for flotation	General dilution ventilation; personal protective equipment
Use as a grain fumigant	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorobromomethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorobromomethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorobromomethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorobromomethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlorobromomethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorobromomethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Chlorobromomethane may be disposed of by absorbing it in vermiculite, dry sand, earth, or a similar material, and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR CHLOROBROMOMETHANE

Condition	**Minimum Respiratory Protection*** **Required Above 200 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORODIFLUOROMETHANE

INTRODUCTION

This guideline summarizes pertinent information about chlorodifluoromethane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CHClF_2$

- **Synonyms**

Algeon 22; CFC 22; difluorochloromethane; difluoromonochloromethane; Dymel 22; Fluorocarbon-22; Freon 22; Genetron 22; monochlorodifluoromethane; refrigerant 22; Ucon 22

- **Identifiers**

1. CAS No.: 75-45-6
2. RTECS No.: PA6390000
3. DOT UN: 1018 12
4. DOT label: Nonflammable gas

- **Appearance and odor**

Chlorodifluoromethane is a colorless, odorless, nonflammable gas; however, it may be shipped as a liquefied gas under pressure or reduced temperature.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 86.47
2. Boiling point (760 mm Hg): -40.8°C (-41.4°F)
3. Specific gravity (water = 1): 1.49 at -69°C (-92.2°F)
4. Vapor density (air = 1 at boiling point of chlorodifluoromethane): 2.98
5. Melting point: -146°C (-230.8°F)
6. Vapor pressure at 21°C (70°F): 7,121.2 mm Hg
7. Solubility: Very soluble in water; soluble in ether, acetone, and chloroform
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: Contact of chlorodifluoromethane at high temperatures with alkalies or alkaline earth

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metals such as aluminum, sodium, potassium, or zinc causes thermal decomposition.

3. Hazardous decomposition products: Toxic gases (such as fluorine, chlorine, phosgene, and carbonyl halides) may be released in a fire involving chlorodifluoromethane.

4. Special precautions: Corrosion can occur when magnesium alloys or aluminum containing more than 2% magnesium is used with fluorocarbon systems in which water may be present.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to chlorodifluoromethane; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chlorodifluoromethane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chlorodifluoromethane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorodifluoromethane. Structural firefighters' protective clothing may provide limited protection against fires involving chlorodifluoromethane.

XPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorodifluoromethane [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1,000 ppm (3,500 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 1,250 ppm (4,375 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure limit that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorodifluoromethane a threshold limit value (TLV) of 1,000 ppm (3,540 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of cardiac sensitization, asphyxiation, and central nervous system effects associated with exposure to chlorodifluoromethane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorodifluoromethane can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chlorodifluoromethane causes depression of the central nervous system, cardiac arrhythmias, and asphyxiation. The LC_{50} in the rat is 35 parts per hundred (pph) (350,000 ppm) for a 15-min exposure; acutely poisoned animals exhibited altered sleep times, stumbling, and respiratory depression before death [NIOSH 1989]. Mice exposed for 2-hr periods showed a maximum tolerated concentration of 320,000 ppm, and a minimum fatal level of 370,000 ppm [ACGIH 1991]. Rats and guinea pigs exposed by inhalation to airborne concentrations of 75,000 to 100,000 ppm chlorodifluoromethane for 2-hr showed excitation and/or changes in equilibrium; narcosis occurred at 200,000 ppm and death occurred at 300,000 and

400,000 ppm [ACGIH 1991]. Dogs exposed to a 50,000-ppm concentration of chlorodifluoromethane developed cardiac sensitization; exposure to 25,000 ppm did not cause this effect [ACGIH 1991]. The minimum concentration capable of altering the reflex response in rabbits varied between 11,000 and 20,000 ppm [ACGIH 1991]. In 2-hr exposures to guinea pigs, the highest concentration tested (200,000 ppm) did not cause death, while 50,000 ppm produced mild clinical changes, and minimal effects were noted at 25,000 ppm [ACGIH 1991]. In a 4-week study in which rats, guinea pigs, dogs, and cats were exposed to a 50,000-ppm concentration of chlorodifluoromethane for twenty 3.5-hr episodes, no clinical, biochemical, or pathological effects were observed [ACGIH 1991]. Rats, mice, and rabbits were exposed for 6 hr/day, 6 days/week for 10 months to 14,000 ppm chlorodifluoromethane. In another experiment, rats and mice were exposed to 2,000 ppm of this substance for the same period. No effects were noted in animals exposed at the lower concentration, but at 14,000 ppm, alterations occurred in body weight, physiological endurance, and hematological characteristics; pathological changes were noted in the lungs, central nervous system, heart, liver, kidneys, and spleen [ACGIH 1991]. In one inhalation bioassay in rats, males exposed to the highest concentration administered showed only a marginal increase in the incidence of subcutaneous fibrosarcomas and Zymbal-gland tumors, and negative results were obtained for females [IARC 1987]. Based on this study, the International Agency for Research on Cancer (IARC) has concluded that the evidence for chlorodifluoromethane's carcinogenicity in animals is limited [IARC 1987].

2. *Effects on Humans:* In humans, chlorodifluoromethane can affect the heart; at very high concentrations, it is an asphyxiant. A study of hospital personnel exposed to 300 ppm chlorodifluoromethane during tissue freezing procedures revealed a 3.5-fold increase in the incidence of palpitations in exposed individuals over the incidence in nonexposed hospital personnel [Clayton and Clayton 1981; Hathaway et al. 1991]. An epidemiologic study involving workers exposed to chlorofluorocarbons, including chlorodifluoromethane, showed no increased mortality due to heart, circulatory, or malignant disorders [Hathaway et al. 1991]. A small study of 539 refrigeration workers exposed to a mixture of chlorofluorocarbons, including chlorodifluoromethane, for at least 6 months and followed for up to 30 years was inconclusive, leading IARC to conclude that the evidence for the carcinogenicity of this substance in humans is inadequate [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Chlorodifluoromethane may cause dizziness, disorientation, incoordination, narcosis, nausea, vomiting, heart palpitations (irregular heart beat), tightness in the chest, and difficult breathing. Direct tissue contact with liquid chlorodifluoromethane may cause frostbite.

2. *Chronic exposure:* Continued low-level exposure to chlorodifluoromethane may cause an irregular heartbeat.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of frostbite, toxicity, or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* If tissue is frozen, seek medical attention ***immediately***; do not rub the affected areas or flush them with water. If tissue is not frozen, immediately and thoroughly wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from fur-

ther exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorodifluoromethane and may result in worker exposures to this substance:

—Formulation of aerosol propellants (former use)

—Use as a component of fluorocarbon resins (such as tetrafluoroethylene polymers) and as a low-temperature solvent

—Use in central air conditioning systems and heat pumps

—Use in cylinder packing and shipping and tank car filling

The following methods are effective in controlling worker exposures to chlorodifluoromethane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chlorodifluoromethane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the cardiovascular system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorodifluoromethane at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the cardiovascular system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorodifluoromethane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorodifluoromethane on the cardiovascular system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chlorodifluoromethane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorodifluoromethane is determined by using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.05 liter/min or less until a maximum air volume of 1 liter is collected. The sample is then treated with carbon disulfide to extract the chlorodifluoromethane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1991].

PERSONAL HYGIENE

If liquid chlorodifluoromethane contacts the skin, workers should flush the affected areas immediately with plenty of tepid water for 15 min, and then wash with soap and water.

Clothing contaminated with liquid chlorodifluoromethane should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles cylinders of liquid chlorodifluoromethane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorodifluoromethane is handled, processed, or stored.

STORAGE

Chlorodifluoromethane should be stored in a cool, dry, well-ventilated area in closed, pressurized, steel containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorodifluoromethane should be protected from physical damage and should be stored separately from alkaline earth metals (such as sodium, aluminum, or potassium), heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorodifluoromethane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chlorodifluoromethane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chlorodifluoromethane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorodifluoromethane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chlorodifluoromethane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorodifluoromethane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with liquid chlorodifluoromethane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against chlorodifluoromethane and have demonstrated resistance: Natural rubber and neoprene. Nitrile, polyvinylchloride, and styrene-butadiene rubber have demonstrated poor resistance to permeation by chlorodifluoromethane.

If liquid chlorodifluoromethane is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which liquid chlorodifluoromethane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with liquid chlorodifluoromethane. Contact lenses should not be worn if the potential exists for chlorodifluoromethane exposure.

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Occupational Health Guideline for Chlorodiphenyl (42% Chlorine)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_7Cl_3$ (approximately)
- Synonyms: Polychlorinated biphenyl; PCB
- Appearance and odor: Colorless to dark liquid with a mild hydrocarbon odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorodiphenyl (42% chlorine) is 1 milligram of chlorodiphenyl (42% chlorine) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for polychlorinated biphenyls be reduced to 1.0 microgram per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week, and that chlorodiphenyl (42% chlorine) be regulated as an occupational carcinogen. The NIOSH Criteria Document for Polychlorinated Biphenyls should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorodiphenyl (42% chlorine) can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Chlorodiphenyl (42% chlorine) may cause irritation of the eyes, nose, and throat, and an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice. Repeated skin contact with the liquid may cause skin irritation. The production of liver tumors and adverse reproductive effects has been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorodiphenyl (42% chlorine).

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorodiphenyl (42% chlorine) at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and skin should be stressed. The skin should be examined for evidence of chronic disorders. Women in the work force should be advised of the potential adverse effects of chlorodiphenyl (42% chlorine) on the unborn child. Those who have borne children and work with chlorodiphenyl (42% chlorine) should be counseled concerning the advisability of nursing their offspring.

—Liver function tests: Chlorodiphenyl (42% chlorine) may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chlorodiphenyl (42% chlorine) is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

- **Summary of toxicology**

Chlorodiphenyl (42% chlorine) vapor is toxic to the liver and causes an acne-form dermatitis (chloracne). Guinea pigs died at intervals up to 21 days after the first of 11 daily applications of 34.5 mg to the skin and, at necropsy, the liver showed fatty degeneration and central atrophy; rats, however, survived 25 daily applications, and only slight changes in the liver were observed. The vapor and liquid are moderately irritating to eye tissues. Cases of mild to moderate skin irritation with an acne-form eruption have been reported in workers exposed to 0.1 mg/m^3; levels of 10 mg/m^3 were unbearably irritating. Several deaths due to atrophy of the liver have occurred among workers exposed to the fumes of chlorodiphenyls and chloronaphthalenes. The production of liver tumors and adverse reproductive effects has been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 257.5 (approximately)
2. Boiling point (760 mm Hg): 325 – 366 C (617 – 691 F)
3. Specific gravity (water = 1): 1.38
4. Vapor density (air = 1 at boiling point of chlorodiphenyl (42% chlorine)): 8.9
5. Melting point: –19 C (-2 F) (pour point)
6. Vapor pressure at 20 C (68 F): 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorodiphenyl (42% chlorine).
4. Special precautions: Chlorodiphenyl (42% chlorine) will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 176 C (349 F)
2. Autoignition temperature: None to boiling point
3. Flammable limits in air, % by volume: Not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

According to the AIHA *Hygienic Guide*, chlorodiphenyl (42% chlorine) has a typical aromatic odor and causes eye irritation. For the purposes of this guideline, however, it is treated as a material with poor warning properties, as no quantitative data are available concerning its odor and irritation thresholds. As stated in the AIHA *Hygienic Guide*, the vapors of the chlorodiphenyls are "moderately irritating to eye tissues." The concentrations causing eye irritation are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorodiphenyl (42% chlorine) on a glass fiber filter connected in a series with a midget bubbler containing iso-octane, followed by gas chromatographic analysis. A detailed analytical method for chlorodiphenyl (42% chlorine) may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set 2" (order number PB 271

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorodiphenyl (42% chlorine).

- Clothing contaminated with liquid chlorodiphenyl (42% chlorine) should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorodiphenyl (42% chlorine) from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorodiphenyl (42% chlorine), the person performing the operation should be informed of chlorodiphenyl's (42% chlorine) hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid chlorodiphenyl (42% chlorine) should be removed promptly and not reworn until the chlorodiphenyl (42% chlorine) is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorodiphenyl (42% chlorine) may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid chlorodiphenyl (42% chlorine) should be promptly washed or showered with soap or mild detergent and water to remove any chlorodiphenyl (42% chlorine).
- Eating and smoking should not be permitted in areas where liquid chlorodiphenyl (42% chlorine) is handled, processed, or stored.
- Employees who handle liquid chlorodiphenyl (42% chlorine) should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to chlorodiphenyl (42% chlorine) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorodiphenyl (42% chlorine) may occur and control methods which may be effective in each case:

Operation	Controls
Use as high-temperature transfer medium in chemical/food processing vessels and drying ovens	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a dielectric in manufacture of transformers, capacitors, resistors, and other electrical apparatus	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application and formulation as plasticizer, flame-retardant, and adhesive and weatherizer in spray surface coatings; manufacture and application of impregnants for cloth, paper, fiberboard, wood, and asbestos; manufacture and application of natural and synthetic waxes and polishes; manufacture and application of hot-melt and other adhesives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as non-flammable working fluid in vacuum pumps, hydraulic systems, and expansion systems	General dilution ventilation; local exhaust ventilation
Use during application of high-pressure, temperature, and moisture lubricants	Personal protective equipment
Use in compounding and processing of plastics for flame retardancy	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture and application for use as pesticides and fungicides	Personal protective equipment
Use as an intermediate or raw material in further organic synthesis	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as sealer for gaskets of natural rubber and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as adhesive release on tapes and ink release on carbonless duplicating paper; as a pigment carrier in dyeing polyesters and paper	Personal protective equipment

Use as a pressure adhesive for sign backings, insect traps, and tapes	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in compounding mastics, and sealing and caulking materials; use in compounding of printing inks	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorodiphenyl (42% chlorine) gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorodiphenyl (42% chlorine) gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorodiphenyl (42% chlorine) soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorodiphenyl (42% chlorine), move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlorodiphenyl (42% chlorine) has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorodiphenyl (42% chlorine) is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Chlorodiphenyl (42% chlorine) may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974, and Volume 18, 1978.

RESPIRATORY PROTECTION FOR CHLORODIPHENYL (42% CHLORINE)

Condition	**Minimum Respiratory Protection*** **Required Above 1 mg/m³**
Vapor Concentration	
10 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against pesticides. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorodiphenyl (42% chlorine); however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorodiphenyl (54% Chlorine)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_5Cl_5$ (approximately)
- Synonyms: Polychlorinated biphenyl; PCB
- Appearance and odor: Pale yellow viscous liquid with a mild hydrocarbon odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorodiphenyl (54% chlorine) is 0.5 milligram of chlorodiphenyl (54% chlorine) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for polychlorinated biphenyls be reduced to 1.0 microgram per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week, and that chlorodiphenyl (54% chlorine) be regulated as an occupational carcinogen. The NIOSH Criteria Document for Polychlorinated Biphenyls should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorodiphenyl (54% chlorine) can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Chlorodiphenyl (54% chlorine) may cause irritation of the eyes, nose, and throat, and an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice. Repeated skin contact with the liquid may cause skin irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorodiphenyl (54% chlorine). The production of liver tumors and adverse reproductive effects have been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorodiphenyl (54% chlorine) at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and skin should be stressed. Women in the work force should be advised of the potential adverse effects of chlorodiphenyl (54% chlorine) on the unborn child. Those who have borne children and work with chlorodiphenyl (54% chlorine) should be counseled concerning the advisability of nursing their offspring.

—Liver function tests: Chlorodiphenyl (54% chlorine) may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chlorodiphenyl (54% chlorine) is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Summary of toxicology**

Chlorodiphenyl (54% chlorine) vapor is toxic to the liver. Rats exposed to 5.4 mg/m³ for 7 hours daily for 4 months showed increased liver weight and injury to the liver cells; 1.5 mg/m³ for 7 months also produced histopathologic evidence of liver damage, which was considered to be of a reversible character. The vapor and the liquid are moderately irritating to the eye; contact with skin leads to removal of natural fats and oils with subsequent drying and cracking of the skin. Acne-form dermatitis (chloracne) due to exposure to chlorodiphenyl of 54% chlorine content has been reported but the period of exposure was not indicated. The production of liver tumors and adverse reproductive effects has been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 326 (approximately)
2. Boiling point (760 mm Hg): 365– 390 C (689–734 F)
3. Specific gravity (water = 1): 1.5
4. Vapor density (air = 1 at boiling point of chlorodiphenyl (54% chlorine)): 11.2
5. Melting point: 10 C (50 F) (pour point)
6. Vapor pressure at 20 C (68 F): 0.00006 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorodiphenyl (54% chlorine).
4. Special precautions: Chlorodiphenyl (54% chlorine) will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 222 C (432 F)
2. Autoignition temperature: None to boiling point
3. Flammable limits in air, % by volume: Not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

Although chlorodiphenyl (54% chlorine) has a typical aromatic odor and causes eye irritation, this substance is treated as a material with poor warning properties, as no quantitative information is available concerning its odor and irritation thresholds. The AIHA *Hygienic Guide* states that the vapors of the chlorodiphenyls are "moderately irritating to eye tissues," but the concentrations which cause irritation are not stated.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorodiphenyl on a filter with subsequent extraction with petroleum ether and gas chromatographic analysis. An analytical method for chlorodiphenyl (54% chlorine) is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorodiphenyl (54% chlorine).
- Clothing contaminated with liquid chlorodiphenyl (54% chlorine) should be placed in closed containers for storage until it can be discarded or until provision is

made for the removal of chlorodiphenyl (54% chlorine) from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorodiphenyl (54% chlorine), the person performing the operation should be informed of chlorodiphenyl's (54% chlorine) hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid chlorodiphenyl (54% chlorine) should be removed promptly and not reworn until the chlorodiphenyl (54% chlorine) is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorodiphenyl (54% chlorine) may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid chlorodiphenyl (54% chlorine) should be promptly washed or showered with soap or mild detergent and water to remove any chlorodiphenyl (54% chlorine).
- Eating and smoking should not be permitted in areas where liquid chlorodiphenyl (54% chlorine) is handled, processed, or stored.
- Employees who handle liquid chlorodiphenyl (54% chlorine) should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to chlorodiphenyl (54% chlorine) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorodiphenyl (54% chlorine) may occur and control methods which may be effective in each case:

Operation	Controls
Use as high-temperature transfer medium in chemical/food processing vessels and drying ovens	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a dielectric in manufacture of transformers, capacitors, resistors, and other electrical apparatus	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application and formulation as plasticizer, flame-retardant, and adhesive and weatherizer in spray surface coatings; manufacture and application of impregnants for cloth, paper, fiberboard, wood, and asbestos; manufacture and application of natural and synthetic waxes and polishes; manufacture and application of hot-melt and other adhesives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as non-flammable working fluid in vacuum pumps, hydraulic systems, and expansion systems	General dilution ventilation; local exhaust ventilation
Use during application of high-pressure, temperature, and moisture lubricants	Personal protective equipment
Use in compounding and processing of plastics for flame retardancy	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture and application for use as pesticides and fungicides	Personal protective equipment
Use as an intermediate or raw material in further organic synthesis	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as sealer for gaskets of natural rubber and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as adhesive release on tapes and ink release on carbonless duplicating paper; as a pigment carrier in dyeing polyesters and paper	Personal protective equipment

Use as a pressure adhesive for sign backings, insect traps, and tapes	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in compounding mastics, and sealing and caulking materials; use in compounding of printing inks	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorodiphenyl (54% chlorine) gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorodiphenyl (54% chlorine) gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If chlorodiphenyl (54% chlorine) soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorodiphenyl (54% chlorine), move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlorodiphenyl (54% chlorine) has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorodiphenyl (54% chlorine) is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Chlorodiphenyl (54% chlorine) may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on chlorodiphenyl (54% chlorine), look up chlorodiphenyl (54% chlorine) in the following documents:

- Medical Surveillance from the SCP
- Respiratory Protection from the SCP
- Personal Protection and Sanitation from the SCP
- NIOSH Criteria Document for Polychlorinated Biphenyls (September 1977)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chlorodiphenyl (54% Chlorine)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974, and Volume 18, 1978.

RESPIRATORY PROTECTION FOR CHLORODIPHENYL (54% CHLORINE)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m^3
Vapor Concentration	
5 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5 mg/m^3** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against pesticides. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorodiphenyl (54% chlorine); however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 5 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chloroform*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CHCl_3$
- Synonyms: Trichloromethane
- Appearance and odor: Colorless liquid with a pleasant, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chloroform is a ceiling level of 50 parts of chloroform per million parts of air (ppm). This may also be expressed as 240 milligrams of chloroform per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 2 ppm averaged over a one-hour period, and that chloroform be regulated as an occupational carcinogen. The NIOSH Criteria Document for Chloroform should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloroform can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Chloroform vapor may cause headache, drowsiness, vomiting, dizziness, unconsciousness, irregular heart beat, and death. Liver and kidney damage may also result from exposure to chloroform vapor. When splashed in the eye, chloroform causes pain and irritation. Swallowing chloroform is followed immediately by severe burning of the mouth and throat, pain in the chest and abdomen, and vomiting. Depending on the amount swallowed, loss of consciousness and liver damage may follow.
2. *Long-term Exposure:* Prolonged exposure to chloroform may cause liver and kidney damage. Prolonged or repeated skin contact with the liquid may produce skin irritation.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chloroform.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chloroform at potentially hazardous levels:

1. *Initial Medical Examination:*

— A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. A history of, or physical signs consistent with, chronic alcoholism probably constitutes such an increased risk. Examination of liver, kidneys, and heart should be stressed. The skin should be examined for evidence of chronic disorders.

— Liver function tests: A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

— Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chloroform vapor is a central nervous system depressant and is toxic to the liver and kidneys. It has been largely abandoned as an anesthetic agent because of the frequency of cardiac arrest during surgery and of

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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delayed death due to hepatic injury. An increased incidence of cardiac arrhythmias has been demonstrated during surgery in patients anesthetized with chloroform, as compared with other anesthetic agents; vapor concentrations were of the order of 22,500 ppm. Animals showed minor and reversible injury of liver and kidneys after repeated 7-hour exposures to concentrations of chloroform as low as 25 ppm, while 50 to 85 ppm produced more severe injury. Experimental human exposures showed that 14,000 to 16,000 ppm caused rapid loss of consciousness in man; 4100 ppm or less caused serious disorientation, while single exposures of 1000 ppm caused dizziness, nausea, and aftereffects of fatigue and headache. Prolonged exposure to 80 to 240 ppm caused lassitude, digestive disturbances, and mental dullness, while 20 to 70 ppm produced milder symptoms. Of 68 chemical workers exposed regularly to concentrations of 2 to 205 ppm for 1 to 4 years, some 25% had hepatomegaly. This group of 68 exposed workers were found to be more susceptible to viral hepatitis than the general population. The hepatotoxicity of several chlorinated hydrocarbons has been shown to be potentiated by prior exposure to some aliphatic alcohols. This phenomenon has been demonstrated in mice exposed first to isopropyl alcohol by gavage and then to chloroform by intraperitoneal injection. A potentiating effect of ethyl alcohol ingestion on the toxicity of chloroform vapor in the occupational setting is suspected, but has not been proven in industrial practice. High concentrations of vapor cause conjunctival irritation and blepharospasm. Liquid chloroform splashed in the eye causes immediate burning pain and conjunctival irritation; the corneal epithelium may be injured, but regeneration is prompt, and the eye returns to normal in 1 to 3 days. The liquid has a defatting effect on the skin and may produce chronic irritation with drying and cracking. Liver tumors have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 119.4
2. Boiling point (760 mm Hg): 61 C (142 F)
3. Specific gravity (water = 1): 1.49
4. Vapor density (air = 1 at boiling point of chloroform): 4.1
5. Melting point: −63.5 C (−82 F)
6. Vapor pressure at 20 C (68 F): 160 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8
8. Evaporation rate (butyl acetate = 1): 11.6

- **Reactivity**

1. Conditions contributing to instability: In the presence of air and light, chloroform slowly reacts to form toxic phosgene and hydrogen chloride gases.
2. Incompatibilities: Chloroform reacts with strong caustics and chemically active metals such as aluminum, magnesium powder, sodium, or potassium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when chloroform decomposes.
4. Special precautions: Liquid chloroform will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Patty reports that the odor threshold of chloroform is approximately 200 to 300 ppm, and May reports an odor threshold of 200 ppm. The *Hygienic Guide*, however, gives an odor threshold of 50 ppm and states that "olfactory fatigue" occurs upon exposure.
2. Eye Irritation Level: Grant states that "in conscious individuals high concentrations of vapors of chloroform cause moderate sensation of stinging and irritation of the eyes, automatically inducing protective closure of the lids." The concentrations causing eye irritation are not mentioned. However, Patty does not give any indication that eye irritation occurs at concentrations even as high as 4096 ppm.
3. Evaluation of Warning Properties: Since there are no quantitative data relating the irritant effects of chloroform to air concentrations, and since olfactory fatigue occurs during exposure to chloroform, this material is treated as a substance with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **One-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average one-hour exposure is based on a single one-hour sample. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chloroform. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chloroform may be used. An analytical method for chloroform is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid chloroform, where skin contact may occur.
- Clothing wet with liquid chloroform should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chloroform from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chloroform, the person performing the operation should be informed of chloroform's hazardous properties.
- Non-impervious clothing which becomes wet with liquid chloroform should be removed promptly and not reworn until the chloroform is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chloroform may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to chloroform, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid chloroform should be promptly washed or showered with soap or mild detergent and water to remove any chloroform.
- Eating and smoking should not be permitted in areas where liquid chloroform is handled, processed, or stored.
- Employees who handle liquid chloroform should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.
- Areas in which exposure to chloroform may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chloroform may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of fluorocarbons for refrigerant propellants; manufacture of fluorocarbon resins	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an extractant solvent in manufacure of pharmaceuticals, rubber, essential oils and flavors, sterols and alkaloids, and in the recovery of fat from waste products	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in chemical analysis and assays; veterinary uses, and in standard solutions as preservative and bactericide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a general solvent in plastics, dyes, oils, waxes, rubber, cleaning and dry cleaning industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in dye, drug, and pesticide industries	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chloroform gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If burning is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chloroform gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chloroform soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chloroform, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chloroform has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chloroform is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

ADDITIONAL INFORMATION

To find additional information on chloroform, look up chloroform in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Chloroform (Revised June 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 1, 1972.

RESPIRATORY PROTECTION FOR CHLOROFORM

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR bis-CHLOROMETHYL ETHER POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about bis-chloromethyl ether for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2H_4Cl_2O$
- **Structure:** $ClCH_2OCH_2Cl$
- **Synonyms:** bis(Chloromethyl) ether; bis-CME; chloro-(chloromethoxy) methane; chloromethyl ether; sym-dichlorodimethyl ether; sym-dichloromethyl ether; dimethyl-1′-dichloroether; oxybis(chloromethane)
- **Identifiers:** CAS 542-88-1; RTECS KN1575000; DOT 2249, label required: "Poison, Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a suffocating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.96
2. Boiling point (at 760 mmHg): 106°C (223°F)
3. Specific gravity (water = 1): 1.315
4. Vapor density (air = 1 at boiling point of bis-chloromethyl ether): 3.97
5. Melting point: -41.5°C (-42.7°F)

- **Reactivity**

1. Incompatibilities: bis-Chloromethyl ether is very volatile and may cause fire if exposed to excessive heat; bis-chloromethyl ether hydrolyzes in water to form hydrogen chloride and formaldehyde.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide, hydrogen chloride, and formaldehyde) may be released in a fire involving bis-chloromethyl ether.
3. Caution: Hydrogen chloride and formaldehyde react to form bis-chloromethyl ether under certain conditions of temperature and humidity. Any reaction in which these two compounds are present should be investigated for bis-chloromethyl ether formation.

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for bis-chloromethyl ether; however, the OSHA standard requires implementation of stringent controls wherever bis-chloromethyl ether or solid or liquid mixtures containing at least 0.1% by weight or volume of bis-chloromethyl ether are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations 29 CFR 1910.1008, bis-Chloromethyl Ether. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated bis-chloromethyl ether as an A-1 substance (confirmed human carcinogen) having a TLV of 0.001 parts of bis-chloromethyl ether per million parts of air (ppm) [0.005 milligram per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek.

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HEALTH HAZARD INFORMATION

• Routes of exposure
bis-Chloromethyl ether may cause adverse health effects following exposure via inhalation, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* Acute inhalation of bis-chloromethyl ether vapor by rats or hamsters caused pulmonary congestion, edema, and hemorrhage. Chronic inhalation of bis-chloromethyl ether by rats or mice produced cancers of the lungs, nasal cavity, or skin.
2. *Effects on humans:* Chronic inhalation of bis-chloromethyl ether has produced lung cancer and a reduction in pulmonary function.

• Signs and symptoms of exposure
1. *Short-term (acute):* bis-Chloromethyl ether vapor is highly irritating to the skin and eyes and to the mucous membranes of the respiratory tract. Liquid bis-chloromethyl ether can cause burns and tissue destruction (necrosis).
2. *Long-term (chronic):* Inhalation of bis-chloromethyl ether can cause breathing difficulty (dyspnea), wheezing, pulmonary hemorrhage, and increased bronchial secretions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to bis-chloromethyl ether, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to bis-chloromethyl ether. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and lung dysfunction.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to bis-chloromethyl ether. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function. Because bis-chloromethyl ether is highly irritating to the skin and mucous membranes, the examining physician should be cognizant of any changes in the condition of the skin or signs of contact and/or allergic dermatitis.

• Medical practices recommended at the time of job transfer or termination
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to bis-chloromethyl ether may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events
1. Acute SHE's include: Contact and/or allergic dermatitis
2. Delayed-onset SHE's include: Cancer of the trachea, bronchi, and lungs

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting bis-chloromethyl ether vapors with Chromosorb 101 in short tubes followed by desorption with helium through a gas chromatographic column and analysis by mass spectroscopy. Direct-reading devices calibrated to measure bis-chloromethyl ether may also be used if available. Detailed sampling and analytical methods for bis-chloromethyl ether may be found in the *NIOSH Manual of Analytical Methods* (method numbers 213, 220).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory type hoods" or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with bis-chloromethyl ether should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of bis-chloromethyl ether from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of bis-chloromethyl ether's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove bis-chloromethyl ether from materials and equipment. Contaminated materials should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage of use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1008:

Areas where bis-chloromethyl ether is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of bis-chloromethyl ether, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving bis-chloromethyl ether which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of bis-chloromethyl ether into regulated areas, non-regulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of bis-chloromethyl ether shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove bis-chloromethyl ether from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to bis-chloromethyl ether may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for bis-chloromethyl ether

Operations	Controls
During use in the manufacture of ion-exchange resins and polymers; during use as a solvent for polymerization reactions and as a chloromethylation agent in chemical synthesis; during use in the treatment of textiles	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with bis-chloromethyl ether, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to bis-chloromethyl ether, an eye-wash fountain should be provided within the immediate work area for emergency use.

If bis-chloromethyl ether gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to bis-chloromethyl ether, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If bis-chloromethyl ether gets on the skin, wash it immediately with soap and water. If bis-chloromethyl ether penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and before showering.

If bis-chloromethyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing bis-chloromethyl ether, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing bis-chloromethyl ether may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing bis-chloromethyl ether may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for bis-chloromethyl ether

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROMETHYL METHYL ETHER
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about chloromethyl methyl ether for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_5ClO
- **Structure:** $ClCH_2OCH_3$
- **Synonyms:** Methyl chloromethyl ether, CMME, dimethylchloroether
- **Identifiers:** CAS 107-30-2; RTECS KN6650000; DOT 1239, label required: "Flammable Liquid"
- **Appearance:** Clear, colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 80.52
2. Boiling point (at 760 mmHg): 59.1°C (138.6°F)
3. Specific gravity (water = 1): 1.0625
4. Vapor density (air = 1 at boiling point of chloromethyl methyl ether): 2.77
5. Melting point: -103.5°C (-154.3°F)

- **Reactivity**

1. Incompatibilities: Cloromethyl methyl ether will react with surface moisture to evolve hydrogen chloride which is corrosive to metal.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chloromethyl methyl ether.
3. Caution: Technical grade chloromethyl methyl ether may contain 1-8% bis-chloromethyl ether, a potential human carcinogen. Chloromethyl methyl ether decomposes to hydrogen chloride and formaldehyde which can, under proper temperature and humidified conditions, form bis-chloromethyl ether.

- **Flammability**

1. Flash point: -17.8°C (0°F) (open cup)
2. Extinguishant: Dry chemical, foam, or carbon dioxide
3. Class IB Flammable Liquid (29 CFR 1910.106)

- **Warning properties**

1. Eye irritation levels: Chloromethyl methyl ether is severely irritating to the eyes and skin at 100 ppm.
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for chloromethyl methyl ether; however, the OSHA standard requires implementation of stringent controls wherever chloromethyl methyl ether or solid or liquid mixtures containing at least 0.1% by weight or volume of chloromethyl methyl ether are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1006, Methyl Chloromethyl Ether. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated chloromethyl methyl ether as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloromethyl methyl ether may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Chronic subcutaneous injection of mice with chloromethyl methyl ether containing bis-chloromethyl ether produced skin cancer; chronic inhalation produced lung cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans:* Acute exposure to chloromethyl methyl ether vapor has caused corneal damage, pulmonary edema, pulmonary congestion, and pneumonia. Dermal exposure to liquid chloromethyl methyl ether has caused burns and tissue destruction (necrosis). Exposure to technical grade chloromethyl methyl ether, which is commonly contaminated with bis-chloromethyl ether (1-8%), has been associated with an increased incidence of lung cancer.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Inhalation exposure to chloromethyl methyl ether can cause severe respiratory impairment, sore throat, fever, and chills. Chloromethyl methyl ether is also highly irritating to the mucous membranes, eyes, and skin.
2. *Long-term (chronic):* Inhalation of chloromethyl methyl ether can cause coughing, wheezing, blood-stained sputum, breathing difficulty (dyspnea), and weight loss.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to chloromethyl methyl ether, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to chloromethyl methyl ether at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to chloromethyl methyl ether. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to chloromethyl methyl ether may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Cancer of the respiratory tract (trachea, bronchi, and lungs).

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting chloromethyl methyl ether vapors with glass impingers followed by extraction with hexane and analysis by electron-capture gas chromatography. Direct-reading devices calibrated to measure chloromethyl methyl ether may also be used if applicable. A detailed sampling and analytical method for chloromethyl methyl ether may be found in the *NIOSH Manual of Analytical Methods* (method number 220).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with chloromethyl methyl ether should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of chloromethyl methyl ether from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of chloromethyl methyl ether's hazardous properties.

Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove chloromethyl methyl ether from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing. OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1006:

Areas where chloromethyl methyl ether is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of chloromethyl methyl ether, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving chloromethyl methyl ether which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of chloromethyl methyl ether into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of chloromethyl methyl ether shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove chloromethyl methyl ether from materials, equipment, and the decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to chloromethyl methyl ether may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for chloromethyl methyl ether

Operations	Controls
During use in the manufacture of ion-exchange resins and polymers; during use as a solvent for polymerization reactions and as a chloromethylation agent in chemical synthesis; during use in the treatment of textiles	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker had contact with chloromethyl methyl ether, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to chloromethyl methyl ether, an eye-wash fountain should be provided within the immediate work area for emergency use.

If chloromethyl methyl ether gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to chloromethyl methyl ether, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If chloromethyl methyl ether gets on the skin, wash it immediately with soap and water. If chloromethyl methyl ether penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations. OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If chloromethyl methyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing chloromethyl methyl ether, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing chloromethyl methyl ether may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing chloromethyl methyl ether may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for chloromethyl methyl ether

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for 1-Chloro-1-Nitropropane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5CHClNO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with an unpleasant odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1-chloro-1-nitropropane is 20 parts of 1-chloro-1-nitropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of 1-chloro-1-nitropropane per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for 1-chloro-1-nitropropane from 20 ppm to 2 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1-Chloro-1-nitropropane can affect the body if it is inhaled or if it comes in contact with the eyes. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure of animals has produced severe irritation of the lungs with severe breathing difficulties which may be delayed in onset. Liver, heart, kidney, and blood vessel damage were also reported in animals. In addition, eye irritation has been reported in animals.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1-chloro-1-nitropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1-chloro-1-nitropropane at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1-chloro-1-nitropropane exposure.

—Chronic respiratory disease: 1-Chloro-1-nitropropane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1-chloro-1-nitropropane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 1-Chloro-1-nitropropane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 1-Chloro-1-nitropropane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: 1-Chloro-1-nitropropane causes heart damage in animals. In persons with impaired cardiovascular function, the inhalation of 1-chloro-1-nitropropane might cause exacerbation of preexisting disorders.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1-Chloro-1-nitropropane is a pulmonary irritant and causes liver, kidney, and heart damage in animals. Exposure of rabbits to concentrations near 2600 ppm for

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2 hours was fatal, but 2200 ppm for 1 hour was nonlethal; autopsy revealed pulmonary edema, cellular necrosis of the heart, liver, and kidneys, and cellular damage in the brain. At high concentrations there was lacrimation, nasal discharge, and pulmonary rales. No human experience has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 123.5
2. Boiling point (760 mm Hg): 140 C (285 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 1-chloro-1-nitropropane): 4.3
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 5.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.8
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Overheating in closed containers may cause explosions.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, hydrogen chloride, and carbon monoxide) may be released in a fire involving 1-chloro-1-nitropropane.
4. Special precautions: Liquid 1-chloro-1-nitropropane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 62 C (144 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of this substance.
2. Eye Irritation Level: According to the *Handbook of Organic Industrial Solvents*, 1-chloro-1-nitropropane may irritate the eyes.
3. Evaluation of Warning Properties: Since the TLV has been recommended only to "minimize" irritation, for the purposes of this guideline, 1-chloro-1-nitropropane is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 1-chloro-1-nitropropane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1-chloro-1-nitropropane.
- Clothing wet with liquid 1-chloro-1-nitropropane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1-chloro-1-nitropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1-chloro-1-nitropropane, the person performing the operation should be informed of 1-chloro-1-nitropropane's hazardous properties.
- Non-impervious clothing which becomes wet with liquid 1-chloro-1-nitropropane should be removed promptly and not reworn until the 1-chloro-1-nitropropane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 1-chloro-1-nitropropane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 1-chloro-1-nitropropane should be promptly washed or showered with soap or mild detergent and water to remove any 1-chloro-1-nitropropane.
- Eating and smoking should not be permitted in areas where 1-chloro-1-nitropropane is handled, processed, or stored.
- Employees who handle liquid 1-chloro-1-nitropropane should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following partial list includes some common operations in which exposure to 1-chloro-1-nitropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent and anti-gelling agent for rubber cements	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid 1-chloro-1-nitropropane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid 1-chloro-1-nitropropane gets on the skin, wash the contaminated skin using soap or mild detergent and water. If liquid 1-chloro-1-nitropropane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1-chloro-1-nitropropane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid 1-chloro-1-nitropropane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1-chloro-1-nitropropane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. Mix spill of up to one gallon with soda ash, spray with water, let stand in bucket with water for two hours, neutralize with dilute hydrochloric acid, flush to sewer, and wash area of spill with detergent and solution.

- Waste disposal methods:

1-Chloro-1-nitropropane may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. If quantities of up to one gallon, by the treatment described above.

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RESPIRATORY PROTECTION FOR 1-CHLORO-1-NITROPROPANE

Condition	**Minimum Respiratory Protection* Required Above 20 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPENTAFLUOROETHANE

INTRODUCTION

This guideline summarizes pertinent information about chloropentafluoroethane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CClF_2CF_3$

- **Synonyms**

  F-115; Fluorocarbon-115; Freon 115; Genetron 115; Halocarbon 115; monochloropentafluoroethane

- **Identifiers**

  1. CAS No.: 76-15-3
  2. RTECS No.: KH7877500
  3. DOT UN: 1020 12
  4. DOT label: Nonflammable gas

- **Appearance and odor**

  Chloropentafluoroethane is a colorless, odorless, nonflammable gas; it is shipped as a liquefied gas under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 154.47
  2. Boiling point (760 mm Hg): -39.1°C (-38.4°F)
  3. Specific gravity: 5.5 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: -106°C (-222.8°F)
  6. Vapor pressure at 21.1°C (69.8°F): 6,034.4 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol and ether
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: Contact of chloropentafluoroethane at high temperatures with alkalies or alka-

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line earth metals such as powdered aluminum, potassium or zinc causes thermal decomposition.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrochloric or hydrofluoric acid, phosgene, fluorides, and chlorides) may be released in a fire involving chloropentafluoroethane.

4. Special precautions: Corrosion can occur when magnesium alloys or aluminum containing more than 2% magnesium is used with fluorocarbon systems in which water may be present.

Flammability

The National Fire Protection Association has not assigned a flammability rating for chloropentafluoroethane; this substance is a nonflammable gas.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical or carbon dioxide to fight fires involving chloropentafluoroethane.

Fires involving chloropentafluoroethane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropentafluoroethane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropentafluoroethane. Structural firefighters' protective clothing may provide limited protection against fires involving chloropentafluoroethane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloropentafluoroethane [29 CFR 1910.1000, Table Z-1].

- **NIOSH PEL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1,000 ppm (6,320 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropentafluoroethane a threshold limit value (TLV) of 1,000 ppm (6,320 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cardiac, skin, CNS, and respiratory effects associated with exposure to chloropentafluoroethane [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropentafluoroethane can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chloropentafluoroethane affects the heart and respiratory system at very high doses. Early studies in experimental animals showed that inhalation of a chloropentafluoroethane concentration of approximately 200,000 ppm caused confusion, pulmonary irritation, tremors, and, occasionally, coma [NLM 1992]. At a concen-

tration of 190,000 ppm, chloropentafluoroethane caused cessation of respiration (apnea) in rats exposed from 4 to 26 min [NLM 1992]. Rats exposed at 800,000 ppm plus 20% oxygen for 4 hr showed no clinical effects of histopathology. Rats and guinea pigs exposed at 600,000 ppm chloropentafluoroethane in oxygen for 2 hr and guinea pigs exposed at 200,000 ppm chloropentafluoroethane in air for varying intervals up to 2 hr showed no adverse clinical signs [ACGIH 1991]. Studies with anesthetized dogs, rats, and monkeys showed that, under certain conditions, exposures of 100,000 to 200,000 ppm of chloropentafluoroethane may increase blood pressure, accelerate heart rate, cause myocardial depression, or change pulmonary mechanics [ACGIH 1991]. Species differences in sensitivity are great. Monkeys do not show respiratory or circulatory effects when exposed to a 200,000 ppm concentration of chloropentafluoroethane; dogs show no respiratory depression when exposed to 200,000 ppm but do show bronchoconstriction, decreased compliance, sensitization of the heart to epinephrine, tachycardia, myocardial depression, and hypotension when inhaling 100,000 to 250,000 ppm chloropentafluoroethane; rats show bronchospasm, decreased compliance, and respiratory stimulation after inhalation of 100,000 ppm chloropentafluoroethane [Clayton and Clayton 1981; NLM 1992]. Rats, mice, rabbits, and dogs which received 90 exposures, 6 hr daily to 100,000 ppm chloropentafluoroethane showed no adverse effects, and rats, guinea pigs, dogs, and cats exposed to 200,000 ppm chloropentafluoroethane for 3.5 hr/day, 5 days/week for 4 weeks also showed no adverse effects after the cessation of exposure [ACGIH 1991].

2. *Effects on Humans:* In humans, chloropentafluoroethane can affect the heart, central nervous system, and skin. The neurological effects of chlorofluorocarbon exposure were evaluated in 27 refrigeration repair workers and 14 age-matched control workers from a local union of plumbers, pipefitters, and insulation workers. Personal air samples taken on two worker-participants over the course of a typical workshift showed average exposures of 1.4 ppm chlorodifluoromethane and 2.2 ppm chloropentafluoroethane. No peripheral neuropathy was seen among the study subjects, and there was no significant difference in mean nerve conduction velocities between study and reference subjects; however, lightheadedness and palpitations were reported significantly more often by refrigeration repair workers than by controls [NLM 1992]. The defatting effects of fluorocarbons such as chloropentafluoroethane, when in prolonged or repeated contact with the skin, may cause dermatologic problems, and contact of the skin with liquefied chloropentafluoroethane may cause frostbite [Clayton and Clayton 1981; Braker and Mossman 1980].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to chloropentafluoroethane include difficult breathing, dizziness, disorientation, incoordination, narcosis, and nausea or vomiting. Exposure to very high concentrations of this substance may affect the heart, causing irregular heartbeat, which could cause death. Contact of the skin with the evaporating liquid may cause frostbite.

2. *Chronic exposure:* The signs and symptoms of chronic exposure of the skin to chloropentafluoroethane include defatting and dermatitis.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of frostbite, toxicity, or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* If tissue is frozen, seek medical attention ***immediately;*** do not rub the affected areas or flush them with water. If tissue is not frozen, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropentafluoroethane and may result in worker exposures to this substance:

—Use as a refrigerant in home appliances, mobile air conditioning units, and retail food refrigeration systems and chillers

—Use as a chemical intermediate

The following methods are effective in controlling worker exposures to chloropentafluoroethane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chloropentafluoroethane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, cardiovascular system, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropentafluoroethane at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the skin, cardiovascular system, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropentafluoroethane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropentafluoroethane on the skin, cardiovascular system, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropentafluoroethane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloropentafluoroethane is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 2.5 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If liquid chloropentafluoroethane contacts the skin, watch for the development of frostbite. If frostbite occurs, the affected part should be wrapped in woolen material and should then be immersed in warm water until medical help is obtained.

Clothing contaminated with liquid chloropentafluoroethane should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles chloropentafluoroethane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where chloropentafluoroethane is handled, processed, or stored.

STORAGE

Chloropentafluoroethane should be stored in a cool, dry, well-ventilated area in tightly sealed, pressurized containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloropentafluoroethane should be protected from physical damage and should be stored separately from metals, including aluminum, zinc, and beryllium, heat, sparks, and open flame.

LEAKS

In the event of a leak involving chloropentafluoroethane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the leak.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloropentafluoroethane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropentafluoroethane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloropentafluoroethane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloropentafluoroethane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropentafluoroethane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloropentafluoroethane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloropentafluoroethane permeation; however, the following materials have been tested against chemically similar materials (Freon 113) and have withstood permeation for periods greater than 8 hr: nitrile rubber and Teflon®. Since specific test data are not available for chloropentafluoroethane, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloropentafluoroethane.

Safety glasses, goggles, or face shields should be worn during operations in which liquid chloropentafluoroethane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloropentafluoroethane. Contact lenses should not be worn if the potential exists for chloropentafluoroethane exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPICRIN

INTRODUCTION

This guideline summarizes pertinent information about chloropicrin for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CCl_3NO_2

- **Synonyms**

Nitrotrichloromethane, trichloronitromethane, nitrochloroform, Chlor-o-pic, Acquinite, Microlysin, Pic-fume, Profume A, Dolochlor, Larvacide 100

- **Identifiers**

1. CAS No.: 76-06-2
2. RTECS No.: PB6300000
3. DOT UN: 1580 56 (liquid chloropicrin)
4. DOT label: Poison B

- **Appearance and odor**

At room temperature, chloropicrin is a noncombustible, oily, colorless liquid with an intense and penetrating odor. The odor threshold reported for chloropicrin is 1.1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 164.4
2. Boiling point (760 mm Hg): 112°C (234°F)
3. Specific gravity (water = 1): 1.66 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of chloropicrin): 5.7
5. Melting point: -64°C (-83°F) (solidifies)
6. Vapor pressure at 20°C (68°F): 20 mm Hg
7. Solubility: Nearly insoluble in water; soluble in ether, benzene, absolute alcohol, acetic acid, carbon tetrachloride, acetone, methyl alcohol, and carbon disulfide.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, friction, or strong impact may cause chloropicrin to detonate.
2. Incompatibilities: Contact of chloropicrin with strong oxidizers may cause fires or explosions. Chloropicrin also reacts violently with aniline in the presence of heat, alcoholic sodium hydroxide, sodium methoxide, and propargyl bromide.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, chlorine, and carbon monoxide) may be released when chloropicrin is heated to decomposition.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloropicrin; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chloropicrin should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropicrin may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropicrin. Chemical protective clothing that is specifically recommended for chloropicrin may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloropicrin.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chloropicrin is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for chloropicrin [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropicrin a threshold limit value (TLV) of 0.1 ppm (0.67 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye, skin, and respiratory irritation with chloropicrin exposure [NIOSH 1992]. The ACGIH limit is based on the risk of severe eye and pulmonary effects associated with exposure to chloropicrin [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropicrin can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloropicrin is a severe eye, mucous membrane, and lung irritant; it is particularly injurious to the small and medium-size bronchi. The oral LD_{50} in rats is 250 mg/kg, and the LC_{50} in the same species is 14.4 ppm for 4 hours [NIOSH 1993]. Acute poisoning causes pulmonary congestion, hemorrhage, edema, and tissue infiltration [ACGIH 1991]. Rats inhaling chloropicrin for longer test periods (duration unspecified) developed kidney, liver, and muscle damage [ACGIH 1991]. In mice, exposure to a 9-ppm concentration of chloropicrin in air caused a 50-percent decrease in respiratory rate (with ulceration and necrosis of the respiratory tract lining) and moderate lung damage [Hathaway et al. 1991]. A National Cancer Institute bioassay for carcinogenicity in rats and mice administered chloropicrin by gavage yielded inconclusive results [Clayton

and Clayton 1981]. Chloropicrin is weakly mutagenic in bacterial test systems [Hayes and Laws 1991].

2. *Effects on Humans:* Chloropicrin is a lacrimator and a severe irritant of the respiratory system in humans; it also causes severe skin irritation on contact. Chloropicrin was formerly used as a war gas; the gastrointestinal effects associated with exposure caused it to be called "vomiting gas" [Genium 1990]. Splashed into the eye, chloropicrin has caused corneal edema and liquification of the cornea [NLM 1993]. Exposure to a chloropicrin concentration of 15 ppm cannot be tolerated for more than 1 minute, and exposure to 4 ppm for a few seconds is temporarily disabling because it causes severe eye and respiratory irritation [Hathaway et al. 1991]. Exposure to 0.3 to 0.37 ppm chloropicrin for 3 to 30 seconds causes tearing and eye pain, and this substance is also a severe skin irritant [ACGIH 1991; Clayton and Clayton 1981]. Exposure to a 15-ppm concentration of chloropicrin for a few seconds causes respiratory tract injury [Clayton and Clayton 1981]. In humans, exposure to 119 ppm in air for 30 minutes is lethal; death is caused by pulmonary edema [Hathaway et al. 1991]. Twenty-seven workers in a cellulose factory who were exposed to a high (not further specified) concentration of chloropicrin for 3 minutes developed pneumonitis after 3 to 12 hours of irritating coughing and difficulty in breathing; they subsequently developed pulmonary edema and one died [NLM 1993]. Exposure to chloropicrin apparently increases an individual's susceptibility to chloropicrin intoxication on subsequent exposure [Hathaway et al. 1991; Clayton and Clayton 1981]. Sublethal exposures may cause delayed-onset pulmonary edema, and late deaths may occur from secondary infection [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to chloropicrin include severe pain and tearing of the eyes and corneal burns and opacification; burns and redness of the skin; cough, difficulty breathing, and pulmonary edema; and vertigo, nausea, and vomiting.

2. *Chronic exposure:* The signs and symptoms of repeated exposure to chloropicrin include increased susceptibility to the acute effects of this substance and damage to the lungs. Based on effects seen in animals, chronic exposure to chloropicrin may cause enlarged and tender liver, jaundice, elevated liver enzymes, and pus, blood, or protein in the urine.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of chloropicrin! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloropicrin or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropicrin and lead to worker exposures to this substance:

—Use as a fumigant on stored grains, cereals, fruits, nuts, vegetables, tobacco, floral crops, lawns, turf, and ornamentals

—Use as a soil fumigant, disinfectant, and sterilizer for the control of fungi, nematodes, and other injurious organisms

—Use as a chemical intermediate in organic synthesis of dyes (methyl violet) and as an oxidizing agent

—Use as an additive to impart a warning odor to odorless fumigants and gases

—Restricted use as a rodenticide and pesticide

—Formerly, use as a tear gas and as a chemical warfare agent

The following methods are effective in controlling worker exposures to chloropicrin, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

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Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chloropicrin, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropicrin at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropicrin exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropicrin on the respiratory system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropicrin.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne chloropicrin is made using a midget fritted glass bubbler containing 10 milliliters of isopropanol. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography with an ultraviolet detector or by gas chromatography using an electron capture detector. The limit of detection for this procedure is not known. This method is described in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

If chloropicrin contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with chloropicrin should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of chloropicrin, particularly its potential to cause severe eye and skin irritation.

A worker who handles chloropicrin should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloropicrin is handled, processed, or stored.

STORAGE

Chloropicrin should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers of chloropicrin should be protected from physical damage or shock and should be stored separately from strong oxidizers and other incompatible materials. Because containers that formerly contained chloropicrin may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloropicrin, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Ventilate atmosphere to reduce concentrations.
4. Water spray may be used to reduce vapors.
5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the chloropicrin for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloropicrin is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropicrin; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of chloropicrin emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although chloropicrin is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropicrin exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets) should be worn to prevent skin contact with chloropicrin. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material has been recommended for use against permeation by chloropicrin and provides protection for periods greater than 8 hours: Responder. Teflon withstands permeation by chloropicrin for greater than 4 hr but less than 8 hr.

If chloropicrin is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloropicrin might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloropicrin. Contact lenses should not be worn if the potential exists for chloropicrin exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR β-CHLOROPRENE

INTRODUCTION

This guideline summarizes pertinent information about β-chloroprene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- Formula

  C_4H_5Cl

- **Structure**

  H_2C=CClCH=CH_2

- **Synonyms**

  Neoprene; 2-chloro-1,3-butadiene; 2-chlorobutadiene; chloroprene

- **Identifiers**

1. CAS No.: 126-99-8
2. RTECS No.: EI9625000
3. DOT UN: 1991 30
4. DOT label: Flammable liquid

- **Appearance and odor**

  β-Chloroprene is a flammable, colorless liquid with a sharp, bitter odor. The best estimate of the odor threshold for β-chloroprene is 15 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 88.54
2. Boiling point (760 mm Hg): 59.4°C (138.9°F)
3. Specific gravity (water = 1): 0.958 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of β-chloroprene): 3.0
5. Freezing point: -130 C (-202°F)
6. Vapor pressure at 20°C (68°F): 188 mm Hg
7. Solubility: Slightly soluble in water; miscible with ether, acetone, and benzene
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Autoxidation forms an unstable peroxide that catalyzes exothermic polymerization of the monomer.
2. Incompatibilities: Contact of β-chloroprene with liquid or gaseous fluorine causes a violent reaction.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen chloride) may be released in a fire involving β-chloroprene.
4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) for β-chloroprene.

1. Flash point: -20°C (-4°F)
2. Autoignition temperature: -15.6°C (4°F)
3. Flammable limits in air (% by volume): Lower, 4.0; upper, 20.0
4. Extinguishant: Use alcohol foam, dry chemical, carbon dioxide, or water spray to fight fires involving β-chloroprene.

Fires involving β-chloroprene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of β-chloroprene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving β-chloroprene. Chemical protective clothing that is specifically recommended for β-chloroprene may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving β-chloroprene.

XPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for β-chloroprene is 25 ppm (90 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for β-chloroprene is 1 ppm (3.6 mg/m^3) as a ceiling limit [NIOSH 1992]. A worker's exposure to β-chloroprene shall at no time exceed this limit. However, β-chloroprene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned β-chloroprene a threshold limit value (TLV) of 10 ppm (36 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned β-chloroprene a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of lung and skin cancer and reproductive effects associated with exposure to this substance [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to β-chloroprene can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* β-Chloroprene causes eye, skin, and respiratory tract irritation, central nervous system depression, liver damage, and reproductive/developmental effects in experimental animals. Acutely poisoned animals showed inflammation of the eyes and mucous membranes and signs of central nervous system depression before dying of respiratory failure [Hathaway et al. 1991]. The oral LD$_{50}$ is 450 mg/kg in rats and 146 mg/kg in mice [NIOSH 1993]. The lowest lethal concentration in rats is 2,280 ppm for

4 hr [Sax and Lewis 1989]. Rats exposed 6 hr/day, 5 days/week for 4 weeks to a β-chloroprene concentration of 40 ppm showed signs of eye and skin irritation and growth depression; when the concentration was increased to 160 or 625 ppm, the animals showed loss of hair, signs of liver damage, and an increased rate of mortality [Hathaway et al. 1991]. By inhalation, chloroprene caused sterility or impotence in more than 50% of rats and mice exposed for 8 hr to concentrations ranging from 120 to 6,227 ppm (rats) or 12 to 152 ppm (mice) [ACGIH 1991; Hathaway et al. 1991]. Studies of chloroprene's embryotoxicity and teratogenicity have reported conflicting results [ACGIH 1991]. The International Agency for Research on Cancer (IARC) concluded that there was inadequate evidence in experimental animals to classify β-chloroprene's carcinogenicity [IARC 1987].

2. *Effects on Humans:* β-Chloroprene causes eye and skin irritation as well as central nervous system depression and may have reproductive, mutagenic, embryotoxic, and/or carcinogenic effects. In contact with the eyes or skin, chloroprene can cause chemical burns [Hathaway et al. 1991]. One fatality involving a worker exposed for 3 to 4 min to an unspecified chloroprene concentration in an unventilated vessel has been reported [ACGIH 1991; Hathaway et al. 1991]. Exposure to β-chloroprene concentrations ranging from 56 to greater than 334 ppm for a 1-month period was associated with hair loss, personality changes, irritability, extreme fatigue, and unbearable chest pain [Hathaway et al. 1991]. Volunteers exposed to a 973-ppm concentration of chloroprene for 15 min experienced nausea and giddiness; when these subjects performed light exercise during the exposure, they experienced these symptoms within 10 min [ACGIH 1991; Hathaway et al. 1991]. Studies of workers exposed to this substance at concentrations of 5 ppm or less report a significant increase in chromosome aberrations, and reproductive effects have been seen in male workers exposed to 0.28 to 1.94 ppm concentrations of chloroprene [Hathaway et al. 1991]. The wives of these workers also reportedly experienced a threefold excess of miscarriages [Hathaway et al. 1991]. Epidemiological studies of chloroprene-exposed workers have yielded conflicting results in the past; however, a recent study of maintenance workers showed a dose-related increase in the incidence of liver, lung, and lymphatic cancers among these workers [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to β-chloroprene may cause redness and inflammation of the eyes and eyelids, corneal necrosis, skin burns, nausea, dizziness, giddiness, personality changes, headache, irritability, reversible hair loss, insomnia, extreme fatigue, respiratory irritation, and severe chest pains.

2. *Chronic exposure:* Chronic exposure to β-chloroprene may cause effects on spermatogenesis or sperm morphology; increased risk of miscarriage; chromosome aberrations; and cancer of the lung, liver, and lymphatic system.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of β-chloroprene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if β-chloroprene or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The use of β-chloroprene in the manufacturing of neoprene and polychloroprene latex may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to β-chloroprene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to β-chloroprene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory tract, and central nervous system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to β-chloroprene at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, respiratory tract, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to β-chloroprene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of β-chloroprene on the eyes, skin, respiratory tract, or central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for β-chloroprene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne β-chloroprene is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 8 liters is collected. The sample is then treated with carbon disulfide to extract the β-chloroprene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.03 mg/sample. This method is described in NIOSH Method No. 1002 [NIOSH 1984].

PERSONAL HYGIENE

If β-chloroprene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with β-chloroprene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of β-chloroprene, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles β-chloroprene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where β-chloroprene or a solution containing β-chloroprene is handled, processed, or stored.

STORAGE

β-Chloroprene should be stored in a cool (less than -15°C (5°F)), dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Chloroprene must be inhibited to prevent hazardous polymerization. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of β-chloroprene should be protected from physical damage and should be stored separately from fluorine, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle β-chloroprene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained β-chloroprene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving β-chloroprene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the β-chloroprene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  beta-Chloroprene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of β-chloroprene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or otherwise use 10,000 lb or more of β-chloroprene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of β-chloroprene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although β-chloroprene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of β-chloroprene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent any skin contact with β-chloroprene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by β-chloroprene and have demonstrated protection for periods greater than 8 hr: Viton and polyvinyl alcohol.

If β-chloroprene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which β-chloroprene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with β-chloroprene. Contact lenses should not be worn if the potential exists for β-chloroprene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROSTYRENE

INTRODUCTION

This guideline summarizes pertinent information about o-chlorostyrene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_8H_7Cl

- **Structure**

$ClC_6H_4CH{=}CH$

- **Synonyms**

2-Chlorostyrene; ortho-chlorostyrene

- **Identifiers**

1. CAS No.: 2039-87-4
2. RTECS No.: WL4160000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

o-Chlorostyrene is a combustible liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 138.6
2. Boiling point (760 mm Hg): 188.7°C (371.7°F)
3. Specific gravity (water = 1): 1.10 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: -63.15°C (-81.67°F)
6. Vapor pressure at 25°C (77°F): 0.096 mm Hg
7. Solubility: Insoluble in water; soluble in alcohol ether, acetone, petroleum ether, and acetic acid.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks and open flame
2. Incompatibilities: None reported
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine) may be released in a fire involving o-chlorostyrene.
4. Special precautions: None reported

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- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for o-chlorostyrene; however, other sources report that this substance is combustible.

1. Flash point: 58.9°C (138°F)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or foam

Fires involving o-chlorostyrene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorostyrene.

XPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for o-chlorostyrene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (285 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 75 ppm (430 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-chlorostyrene a threshold limit value (TLV) of 50 ppm (283 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 75 ppm (425 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The ACGIH limits are based on the risk of liver, kidney, and narcotic effects associated with exposure to o-chlorostyrene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorostyrene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, o-chlorostyrene is toxic to the liver and kidneys. Applied to rabbit skin for 24 hr, 10 mg of o-chlorostyrene caused irritation [Sax and Lewis 1989]. The dermal LD_{50} in rabbits is 20 g/kg [Sax and Lewis 1989]. The instillation of 500 mg into the eyes of rabbits also caused irritation [Sax and Lewis 1989]. The oral LD_{50} in rats is 5.2 g/kg [Sax and Lewis 1989]. A group of 24 rats, 3 rabbits, 12 guinea pigs, and 1 dog of each sex were exposed 7 hr/day, 5 days/week for a total of 130 exposures in 180 days to an analytically determined average o-chlorostyrene concentration of 101 ppm (576 mg/m^3). No adverse effects on appearance, growth, demeanor, mortality, hematology, or blood chemistry values were apparent; at autopsy, no changes in organ weights or gross pathology were evident. However, microscopic examination of the liver and kidney tissues of animals of all four species showed a slightly higher incidence than in controls of changes in these organs [ACGIH 1991].

2. *Effects on Humans:* No toxic effects of o-chlorostyrene exposure have been reported in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Based on effects seen in animals, contact of the skin or eyes with o-chlorostyrene may cause irritation.

2. *Chronic exposure:* Based on effects seen in animals, long-term exposure to o-chlorostyrene may cause hematuria, proteinuria, acidosis, an enlarged liver, jaundice, and elevated liver enzymes.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of o-chlorostyrene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorostyrene or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorostyrene and may result in worker exposures to this substance:

—Use in organic synthesis and in the preparation of specialty polymers

The following methods are effective in controlling worker exposures to o-chlorostyrene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to o-chlorostyrene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and kidneys.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorostyrene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the liver or kidneys.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorostyrene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorostyrene on the liver or kidneys. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-chlorostyrene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorostyrene is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). STEL and TWA samples are both collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 20 liters (TWA) or 3 liters (STEL) is collected. The sample is then treated with carbon disulfide to extract the o-chlorostyrene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If o-chlorostyrene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with o-chlorostyrene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of o-chlorostyrene.

A worker who handles o-chlorostyrene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where o-chlorostyrene or a solution containing o-chlorostyrene is handled, processed, or stored.

STORAGE

o-Chlorostyrene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorostyrene should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained o-chlorostyrene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorostyrene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
6. For large liquid spills, call the local fire department.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorostyrene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-chlorostyrene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorostyrene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorostyrene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorostyrene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with o-chlorostyrene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorostyrene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorostyrene.

If o-chlorostyrene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorostyrene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorostyrene. Contact lenses should not be worn if the potential exists for o-chlorostyrene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROTOLUENE

INTRODUCTION

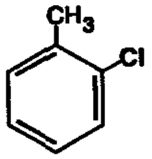
This guideline summarizes pertinent information about o-chlorotoluene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CH_3C_6H_4Cl$

- **Structure**



- **Synonyms**

  2-Chloro-1-methylbenzene; 2-chlorotoluene; 2-methylchlorobenzene; 1-methyl-2-chlorobenzene; *o*-tolyl chloride; Halso 99

- **Identifiers**

  1. CAS No.: 95-49-8
  2. RTECS No.: XS9000000
  3. DOT UN: 2238 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  o-Chlorotoluene is a colorless liquid. The odor threshold for o-chlorotoluene is 0.32 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 126.59
  2. Boiling point (760 mm Hg): 159°C (318.2°F)
  3. Specific gravity (water = 1): 1.083 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of o-chlorotoluene): 4.37
  5. Melting point: -35.1°C (-31.18°F)
  6. Vapor pressure at 43.2°C (109.8°F): 10 mm Hg

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7. Solubility: Slightly soluble in water; freely soluble in alcohol, acetone, ether, benzene, carbon tetrachloride, and chloroform

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of o-chlorotoluene with oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving o-chlorotoluene.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to o-chlorotoluene (unspecified isomer, mixture, or concentration).

1. Flash point: 52°C (126°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, CO_2, water spray, or standard foam to fight fires involving o-chlorotoluene.

Fires involving o-chlorotoluene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of o-chlorotoluene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorotoluene. Structural firefighters' protective clothing may provide limited protection against fires involving o-chlorotoluene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for o-chlorotoluene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) as 50 ppm (250 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 75 ppm (375 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-chlorotoluene a threshold limit value (TLV) of 50 ppm (259 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of moderate skin and eye irritation. The ACGIH limit is based on the risk of eye and skin irritation and systemic poisoning associated with exposure to o-chlorotoluene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorotoluene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

Summary of toxicology

1. *Effects on Animals:* In animals, o-chlorotoluene is irritating to the eyes and skin and, at high doses, this substance affects the central nervous system. A 24-hr patch test with o-chlorotoluene showed moderate skin irritation on both abraded and intact rabbit skin [ACGIH 1991]. Undiluted liquid o-chlorotoluene applied to the skin of guinea pigs under an occlusive dressing in doses of 1 ml/kg or 10 ml/kg for a 24-hr period caused moderately severe local irritation and evidence of skin absorption [ACGIH 1991]. One drop of undiluted o-chlorotoluene instilled into the eye of a rabbit resulted in moderate conjunctival erythema; the cornea was opaque 24 hr after instillation but appeared normal 2 weeks later [ACGIH 1991]. The oral LD_{50} in rats is 5,700 mg/kg, and three of 20 rats died after inhaling approximately 2,400 ppm [EPA 1989]. Rats exposed by inhalation for 6 hr to a 4,000-ppm concentration of o-chlorotoluene lost coordination in 1.5 hr, became prostrate after 1.75 hr, and showed tremors after 2 hr of exposure; marked vasodilation also developed in these animals. All three rats survived, however, and had gained weight (averaging 33 grams) 2 weeks later. Mice, rats, and guinea pigs exposed at a chamber concentration of 4,400 ppm exhibited the following: gasping, ataxia, and convulsions in mice within 30 min after exposure, and gasping, hyperpnea, ataxia, and convulsions in rats and guinea pigs in 45 min. All animals were comatose in 60 min. All mice and rats died as did 7 of 10 guinea pigs. Two guinea pigs were alive 2 week postexposure [ACGIH 1991]. Three rats exposed to 14,000 ppm o-chlorotoluene survived but showed loss of coordination, vasodilation, labored respiration, and narcosis. Of three rats exposed to 175,000 ppm, two were severely incapacitated while the other died. The two that survived were gaining weight 2 weeks later [ACGIH 1991].

2. *Effects on Humans:* There are no reports of the effects of exposure to o-chlorotoluene in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Based on effects seen in animals, acute overexposure to o-chlorotoluene may cause dizziness; loss of coordination; tremors; difficult breathing; redness, inflammation, and tearing of the eyes; and redness and inflammation of the skin.

2. *Chronic exposure:* No signs or symptoms of continued low-level exposure to o-chlorotoluene have been reported.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of o-chlorotoluene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorotoluene or any material containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorotoluene and may result in worker exposures to this substance:

—Use as a solvent and as an intermediate in the production of organic chemicals, pharmaceuticals, synthetic rubber compounds, and dyes

—Use as an intermediate in the production of herbicides

The following methods are effective in controlling worker exposures to o-chlorotoluene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

— Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to o-chlorotoluene, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and central nervous system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorotoluene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorotoluene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorotoluene on the eyes, skin, or central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-chlorotoluene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorotoluene is determined by using a charcoal tube (100/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 20 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is an OSHA modification of NIOSH Method 1003, *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If o-chlorotoluene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with o-chlorotoluene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of o-chlorotoluene, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles o-chlorotoluene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where o-chlorotoluene is handled, processed, or stored.

STORAGE

o-Chlorotoluene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorotoluene should be protected from physical damage and should be stored separately from oxidizing materials, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained o-chlorotoluene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorotoluene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and gently place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the o-chlorotoluene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorotoluene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR Part 355.40] to notify the National Response Center of an accidental release of o-chlorotoluene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorotoluene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorotoluene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorotoluene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves and other protective clothing, as appropriate) should be worn to prevent any skin contact with o-chlorotoluene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Viton® may withstand permeation by o-chlorotoluene for more than 4 but fewer than 8 hr. The following materials have breakthrough times of less than 1 hr and are not recommended for use with o-chlorotoluene: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Saranex.

If o-chlorotoluene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorotoluene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorotoluene.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-CHLORO-6-TRICHLOROMETHYL PYRIDINE

INTRODUCTION

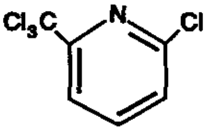
This guideline summarizes pertinent information about 2-chloro-6-trichloromethyl pyridine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_3Cl_4N$

- **Structure**



- **Synonyms**

Nitrapyrin; α,α,α-6-tetrachloro-2-picoline; N-Serve, N-Serve nitrogen stabilizer; Dowco-163

- **Identifiers:**

1. CAS No.: 1929-82-4
2. RTECS No.: US7525000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

2-Chloro-6-trichloromethyl pyridine is a colorless or white, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 230.93
2. Boiling point (11 mm Hg): 136°–137.5°C (276.8°–279.5°F)
3. Specific gravity (water = 1): Data not available
4. Vapor density: Not applicable
5. Melting point: 62.5°–62.9°C (144.5°–145.2°F)
6. Vapor pressure: 0.0028 mm Hg at 23°C (73.4°F)
7. Solubility: Insoluble in water
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Aluminum, magnesium, or their alloys

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving 2-chloro-6-trichloromethyl pyridine.
4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating for 2-chloro-6-trichloromethyl pyridine.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron oxide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2-chloro-6-trichloromethyl pyridine.

XPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for 2-chloro-6-trichloromethyl pyridine are 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limits (RELs) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 20 mg/m^3. The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-chloro-6-trichloromethyl pyridine a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 20 mg/m^3 for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 min [ACGIH 1991].

- **Rationale for limits**

The OSHA limits are based on the risk of physical irritation associated with exposure to 2-chloro-6-trichloromethyl pyridine [54 Fed. Reg. 2592 (1989)].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-chloro-6-trichloromethyl pyridine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, 2-chloro-6-trichloromethyl pyridine is moderately toxic when ingested or absorbed through the skin. The dermal LD_{50} in rabbits is 850 mg/kg [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50}s in rats, mice, and rabbits are 940 mg/kg, 710 mg/kg, and 500 mg/kg respectively [NIOSH 1993; Sax and Lewis 1989]. Dogs and rats fed 15 mg/kg 2-chloro-6-trichloromethyl pyridine daily for 93 days showed no adverse effects on behavior, growth, food consumption, body and organ weights, mortality, or serum chemistries; at autopsy, no gross or microscopic changes to the organs or tissues were detectable [ACGIH 1991]. Male rats fed concentrations of 1,000 ppm in the diet for 2 years had a statistically significant reduction in mean body weight at 12 months, but not at 18 and 24 months. No effects were recorded at lower concentrations. Female rats fed between 30 and 1,000 ppm for 2 years had an increased incidence of bile duct hyperplasia [Dow Chemical USA 1967].

2, *Effects on Humans:* There are no data on the acute or chronic effects of exposure to 2-chloro-6-trichloromethyl pyridine in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to 2chloro-6-trichloromethyl pyridine may irritate the eyes, nose, throat, and skin. Higher levels may cause dizziness and lightheadness.

2. *Chronic exposure:* Chronic exposure to 2-chloro-6-trichloromethyl pyridine may cause dizziness, headaches, loss of appetite and insomnia. Repeated exposure may affect the liver and kidneys.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2-chloro-6-trichloromethyl pyridine or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 2-chloro-6-trichloromethyl pyridine and result in worker exposures to this substance:

—Use as a fertilizer additive to control nitrification and prevent loss of soil nitrogen from land to be planted with corn, cotton, wheat, or sorghum

—Manufacture, formulation, and application of 2-chloro-6-trichloromethyl pyridine-containing products

Methods that are effective in controlling worker exposures to 2-chloro-6-trichloromethyl pyridine, depending on the feasibility of implementation, are:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH:

American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-chloro-6-trichloromethyl pyridine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the kidneys, liver, eyes, and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-chloro-6-trichloromethyl pyridine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) including a history and other findings consistent with diseases of the kidneys, liver, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-chloro-6-trichloromethyl pyridine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-chloro-6-trichloromethyl pyridine on the kidneys, liver, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-chloro-6-trichloromethyl pyridine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

The OSHA method for determining worker exposure to airborne concentrations of 2-chloro-6-trichloromethyl pyridine (total dust) is made using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Particulates not otherwise regulated (Total Dust) [OSHA 1987].

The OSHA method for determining worker exposure to airborne concentrations of 2-chloro-6-trichloromethyl pyridine (respirable fraction) is made using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is preceded by a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Particulates not otherwise regulated (Respirable Fraction) [OSHA 1987].

PERSONAL HYGIENE

If 2-chloro-6-trichloromethyl pyridine contacts the skin, workers should wash the skin with soap and water.

Clothing contaminated with 2-chloro-6-trichloromethyl pyridine should be removed.

A worker who handles 2-chloro-6-trichloromethyl pyridine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or apply cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2-chloro-6-trichloromethyl pyridine or a solution containing 2-chloro-6-trichloromethyl pyridine is handled, processed, or stored.

STORAGE

2-Chloro-6-trichloromethyl pyridine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance should not be stored in unlined containers or be pumped with equipment made of aluminum, magnesium, or alloys of these metals. Containers of 2-chloro-6-trichloromethyl pyridine should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-chloro-6-trichloromethyl pyridine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. No specific information is available on clean-up procedures for spills or leaks involving this substance.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  2-Chloro-6-trichloromethyl pyridine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the National Response Center of an accidental release of 2-chloro-6-trichloromethyl pyridine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-chloro-6-trichloromethyl pyridine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-

261.24. Although 2-chloro-6-trichloromethyl pyridine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-chloro-6-trichloromethyl pyridine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with 2-chloro-6trichloromethyl pyridine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-chloro-6-trichloromethyl pyridine. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-chloro-6-trichloromethyl pyridine.

If 2-chloro-6-trichloromethyl pyridine is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-chloro-6-trichloromethyl pyridine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-chloro-6-trichloromethyl pyridine. Contact lenses should not be worn if the potential exists for 2-chloro-6-trichloromethyl pryidine exposure.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORPYRIFOS

INTRODUCTION

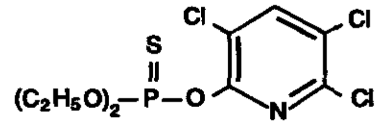
This guideline summarizes pertinent information about chlorpyrifos for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{11}Cl_3NO_3PS$

- **Structure**



- **Synonyms**

Brodan; chloropyrifos-ethyl; O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate; DOWCO 179; Dursban; Lorsban; Pyrinex

- **Identifiers**

1. CAS No.: 2921-88-2
2. RTECS No.: TF6300000
3. DOT UN: 2783 55
4. DOT label: None

- **Appearance and odor**

Chlorpyrifos is a colorless to white, crystalline solid with a mild, mercaptan-like odor. The technical grade often contains volatile contaminants, which are partly responsible for the offensive odor of this substance. Chlorpyrifos is an organophosphate insecticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 350.57
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.398 at 43.5°C (110.3°F) (liquid)
4. Vapor density: Data not available
5. Melting point: 41° to 42°C (105.8° to 107.6°F)
6. Vapor pressure at 25°C (77°F): 0.00002 mm Hg
7. Solubility: Slightly soluble in water; soluble in most organic solvents; slowly hydrolyzed by acid or alkaline solutions
8. Evaporation rate: Data not available

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Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Contact of chlorpyrifos with strong acids (such as hydrochloric, sulfuric, or nitric acid) causes a violent reaction. Contact with acidic or alkaline solutions causes hydrolysis.
3. Hazardous decomposition products: Toxic gases (such as chlorine and the oxides of nitrogen, phosphorus, and sulfur) may be released in a fire involving chlorpyrifos.
4. Special precautions: Chlorpyrifos is corrosive to copper and brass.

Flammability

The National Fire Protection Association has not assigned a flammability rating to chlorpyrifos; however, this substance is combustible.

1. Flash point: 27.8°C (82°F)(Dursban®); 30.6°C (87°F)(Lorsban)(TAG closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving chlorpyrifos.

Fires involving chlorpyrifos should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chlorpyrifos may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Do not scatter this material. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorpyrifos. Chemical protective clothing that is specifically recommended for chlorpyrifos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chlorpyrifos.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorpyrifos [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.6 mg/m^3 as a short-term exposure limit (STEL). The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. The NIOSH REL also bears a Skin notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorpyrifos a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to chlorpyrifos [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to chlorpyrifos.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorpyrifos can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chlorpyrifos is an inhibitor of blood and plasma cholinesterase. The dermal LD$_{50}$ in rabbits is 2,000 mg/kg, and the oral LD$_{50}$ in rats is 82 mg/kg [NIOSH 1990]. Administered to monkeys at doses of 2.0 or 0.4 mg/kg/day for

6 months (route not specified), chlorpyrifos caused inhibition of plasma and red blood cell cholinesterase; at a dose of 0.08 mg/kg/day, only the plasma enzyme was inhibited in these animals [Hayes 1982]. Brain cholinesterase was not affected at any of these doses, and no clinical or morphological effects were noted at autopsy [Hayes 1982]. In 2-year feeding studies in dogs and rats, doses of 1 or 3 mg/kg/day produced depression of plasma and red blood cell cholinesterase; brain cholinesterase was depressed only at the highest dose [Hayes 1982]. In both rats and dogs, even the highest dose (3 mg/kg/day) produced no clinically important effects, as judged by survival, growth, relative and absolute organ weights, blood, urine, and clinical chemical findings, and gross and microscopic pathology [Hayes 1982]. In a three-generation reproduction and fertility study, no teratologic or reproductive effects were seen in male and female rats fed 1 mg/kg/day chlorpyrifos [ACGIH 1991].

2. *Effects on Humans:* In humans, chlorpyrifos is an inhibitor of plasma cholinesterase. The lowest toxic dose in humans is estimated to be 300 mg/kg; this dose caused peripheral nervous system effects, muscular weakness, and coma [NIOSH 1990]. Four repeated chlorpyrifos doses (10 mg/kg each) were applied to the skin of volunteers for a 24-hr period (each application) and caused no plasma cholinesterase depression; however, increasing the dose to 25 mg/kg did produce plasma cholinesterase inhibition, even when the duration of skin contact was reduced to 12 hr [ACGIH 1991]. Human male volunteers given 0.014 or 0.03-mg/kg chlorpyrifos per day for 20 days, followed by 0.1 mg/kg/day for an additional 9 days, showed no adverse behavioral effects or changes in hematology, urinalysis, or biochemistry parameters [Hayes 1982]. At the highest dose, plasma cholinesterase was depressed in these volunteers, but cholinesterase levels returned to normal within 4 weeks of the cessation of exposure. Red blood cell cholinesterase activity was not affected at any level [Hayes 1982]. Five of seven workers applying chlorpyrifos spray with hand-operated power sprayers (0.5% emulsion or 0.25% or 0.5% suspensions of water-wettable powder) had plasma cholinesterase values that were more than 50% below baseline values within 2 weeks after beginning work, and one worker had a plasma enzyme reduction that was greater than 70%. No inhibition of red blood cell cholinesterase was observed in these workers, and there were no signs or symptoms of illness [Hayes 1982; ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to chlorpyrifos depends on the route and extent of exposure. Inhalation can cause respiratory and ocular effects, often within a few minutes of exposure, and may cause a feeling of tightness in the chest, wheezing, laryngeal spasms, excessive salivation, bluish/purplish discoloration of the skin and lips, narrowed pupils, blurred vision, tearing, runny nose, or frontal headache. Ingestion of chlorpyrifos may cause anorexia, nausea, vomiting, abdominal cramps, and diarrhea. Skin absorption may result in localized sweating and muscle tremors in the area where skin absorption took place.

2. *Chronic exposure:* Repeated exposure to concentrations of chlorpyrifos too low to cause signs or symptoms after a single exposure may produce the signs and symptoms of poisoning described above. Continued daily exposure to low doses of chlorpyrifos may cause increasingly severe effects.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air *immediately*. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chlorpyrifos or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorpyrifos and may result in worker exposures to this substance:

—Manufacture, formulation, and application of pesticides containing chlorpyrifos

—Use as an acaricide

—Use as an agricultural insecticide on corn, deciduous fruits and nuts, alfalfa, cotton, sorghum, and citrus crops and as a nonagricultural pesticide for household pests and aquatic larvae

—Use in controlling chinch bugs in Gulf Coast states and in controlling ticks on cattle and sheep in Australia

The following methods are effective in controlling worker exposures to chlorpyrifos, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chlorpyrifos, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood (plasma and red blood cell cholinesterase levels).

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorpyrifos at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the blood. Pre-exposure baseline plasma and red blood cell cholinesterase levels should be established.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorpyrifos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorpyrifos on plasma or red blood cell cholinesterase activity levels. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as chlorpyrifos. RBC ChE is an indicator of both acute and chronic overexposure. The recommended biological exposure index for chlorpyrifos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for preexposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorpyrifos is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.05 and is found in OSHA Method No. 62 in the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If chlorpyrifos contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with chlorpyrifos should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chlorpyrifos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles chlorpyrifos should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorpyrifos or a solution containing chlorpyrifos is handled, processed, or stored.

STORAGE

Chlorpyrifos should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorpyrifos should be protected from physical damage and should be stored separately from strong acids (such as hydrochloric, sulfuric, or nitric acid), heat, sparks, and open flame. Because containers that formerly contained chlorpyrifos may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorpyrifos, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use water spray to reduce vapors.
6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the chlorpyrifos for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chlorpyrifos is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for chlorpyrifos is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorpyrifos emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chlorpyrifos is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorpyrifos exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should only use respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with chlorpyrifos. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chlorpyrifos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated good resistance: laminates of Viton and neoprene or of butyl rubber and neoprene. Since specific test data are not available for chlorpyrifos, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chlorpyrifos.

If chlorpyrifos is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chlorpyrifos might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chlorpyrifos. Contact lenses should not be worn if the potential exists for chlorpyrifos exposure.

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Occupational Health Guideline for Chromic Acid and Chromates*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all chromic acid and chromates. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic acid

- Formula: CrO_3
- Synonyms: Chromic anhydride; chromium trioxide
- Appearance and odor: Dark red, deliquescent, odorless solid.

Sodium dichromate

- Formula: $Na_2Cr_2O_7$-$2H_2O$
- Synonyms: Sodium bichromate (dihydrate)
- Appearance and odor: Red-orange, odorless solid.

Potassium chromate

- Formula: K_2CrO_4
- Synonyms: Chromate of potash
- Appearance and odor: Yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromic acid or chromates is a ceiling of 0.1 milligram of chromic acid or chromates per cubic meter of air (mg/m^3). Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms include the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 Cr (VI) mg/m^3 and that thesecompounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/m^3 averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chromic acid or chromates can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chromic acid mist and chromate dusts may cause severe irritation of the nose, throat, bronchial tubes, and lungs. Chromic acid splashed in the eyes may cause severe injury. If swallowed, chromates and sodium and potassium dichromates may cause stomach and kidney problems. These

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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compounds, if swallowed, often cause vomiting. Skin exposure to chromic acid or chromates may cause ulceration of the skin.

2. Long-term Exposure: Repeated or prolonged exposure to chromic acid or chromate dust or mist may cause an ulceration and perforation of the nasal septum. Respiratory irritation may occur with symptoms resembling asthma. Liver damage with yellow jaundice has been reported. Prolonged or repeated exposure of the skin may cause a skin rash. Allergic skin rash may also occur. An increased amount of lung cancer has been found in employees in the chromate-producing industry.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chromic acid or chromates.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chromic acid or chromates at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to chromic acid or chromates would be expected to be at increased risk from exposure. Examination of the respiratory system, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Chromates have been shown to cause blood changes in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—14" x 17" chest roentgenogram: Chromates may cause human lung damage and are associated with a high incidence of lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chromates are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

—Urinalysis: Since chromates may cause kidney damage, a urinalysis should be obtained, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Chromates may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chromates are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Emphasis should be placed on observation for changes in the mucous membranes of the upper respiratory tract, ulceration of the skin, and surveillance for malignancy of the respiratory tract and lungs.

- **Summary of toxicology**

Chromic acid mist and chromate dusts are severe irritants of the nasopharynx, larynx, lungs, and skin. Chromium compounds, especially the hexavalent compounds are associated with a high incidence of lung cancer in humans. Administered subcutaneously to rabbits and guinea pigs, chromates produce kidney damage, with albuminuria and cylindruria; fatal nephritis occurred in a human treated with chromic acid to cauterize a wound. Workers exposed to chromic acid or chromates in concentrations of 0.11 to 0.15 mg/m^3 developed ulcers of the nasal septum and irritation of the conjunctiva, pharynx and larynx, as well as asthmatic bronchitis. A worker exposed to unmeasured but massive amounts of chromic acid mist for 4 days developed severe frontal headache, wheezing, dyspnea, cough, and pain on inspiration; after 6 months there was still chest pain on inspiration and cough. In an industrial plant where the airborne chromic acid concentrations measured from 0.18 to 1.4 mg/m^3, moderate irritation of the nasal septum and turbinates was observed after 2 weeks of exposure, ulceration of the septum after 4 weeks, and perforation of the septum after 8 weeks. A worker exposed to an unmeasured concentration of chromic acid mist for 5 years developed jaundice and was found to be excreting significant amounts of chromium; liver function in four other workers with high urinary chromium excretion was mildly to moderately impaired. Other studies of chromate workers have not found any unusual incidence of liver diseases or other systemic diseases except for lung cancer. Erosion and discoloration of the teeth has been attributed to chromic acid exposure. Blood changes were observed in chromate plant workers, including leukocytosis or leukopenia, monocytosis, and eosinophilia. A markedly increased incidence of bronchogenic carcinoma occurs in workers exposed to chromate dust. The latent period is relatively short, suggesting the presence of a potent carcinogen. Calcium chromate and zinc chromate have been demonstrated to be carcinogenic in rats, and the risk of lung cancer is reportedly increased in chrome pigment workers. Papillomata of the oral cavity and larynx were found in 15 of 77 chrome platers exposed for an average of 6.6 years to chromic acid mist at air concentrations of chromium of 0.4 mg/m^3. There is no positive evidence that chromic acid in the workplace has contributed to an increase in lung cancer, neither is there definitive evidence that absolves chromic acid. A concentrated solution of chromic acid in the eye causes severe corneal injury; chronic exposure to the mist causes conjunctivitis. Chrome ulcer, a penetrating lesion of the skin, occurs chiefly on the hands and forearms where there has been a break in the epidermis; it is believed to be due to a direct necrotizing effect of the chromate ion. The ulcer is relatively painless, heals slowly, and produces a characteristic depressed scar.

Prolonged exposure to chromic acid mist causes dermatitis, which varies from a dry erythematous eruption to a weeping eczematous condition. Cutaneous sensitization to chromate compounds is a common problem in industrial practice.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Chromic acid**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): Decomposes when it melts
3. Specific gravity (water = 1): 2.7
4. Vapor density (air = 1 at boiling point of chromic acid): Not applicable
5. Melting point: 197 C (387 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Data not available (very low)
7. Solubility in water, g/100 g water at 20 C (68 F): 63
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Sodium dichromate**

1. Molecular weight: 298
2. Boiling point (760 mm Hg): 400 C (752 F) (decomposes)
3. Specific gravity (water = 1): 2.34
4. Vapor density (air = 1 at boiling point of sodium dichromate): Not applicable
5. Melting point: 357 C (674 F) (loses water at 85 C (185 F))
6. Vapor pressure at 20 C (68 F): Zero (except for water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 236
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Potassium chromate**

1. Molecular weight: 194
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 2.7
4. Vapor density (air = 1 at boiling point of potassium chromate): Not applicable
5. Melting point: 971 C (1780 F)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 39
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity—Chromic acid or chromates**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with any combustible, organic, or other readily oxidizable materials such as paper, wood, sulfur, aluminum, plastics, etc. may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: Chromic acid or chromates will attack most forms of metals, cloth, leather, plastics, rubber, and coatings and may cause spontaneous ignition.

- **Flammability**

1. Chromic acid is not combustible in itself, but is a powerful, oxidizing material. It will ignite on contact with acetic acid and alcohol.

- **Warning properties**

Grant states that "contact with the solid material or with concentrated solution (of chromic acid) by splash in the eye causes severe corneal injury characterized by infiltration, vascularization, and opacification of the cornea.

"More commonly, exposure to chromic acid occurs in less serious form as a result of spraying of fine droplets into the air from electroplating baths or by transfer to the eyes on the fingers. After chronic exposure to such conditions, the ocular changes seen are chronic conjunctival inflammation, analogous to the well-known irritation of the nasal mucosa which leads to perforation of the nasal septum." In addition, Grant states that "dichromates (bichromates) as ammonium, sodium, or potassium salts are water-soluble, crystalline substances which have a peculiar injurious effect on the cornea, causing great swelling of the corneal stroma."

The *Documentation of TLV's* states that "Vigliani and Zurlo reported . . . irritation of the mucous membranes of the larynx, pharynx, and conjunctiva . . . in a group of workers allegedly exposed to chromates or chromic acid in concentrations ranging from 0.11 to 0.15 mg/m^3."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chromic acid or chromates. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of chromic acid or chromates on a filter, followed by chemical treatment and colorimetric analysis. An analytical method for chromic acid and chromates is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solids or liquids containing chromic acid or chromates.
- If employees' clothing may have become contaminated with solids or liquids containing chromic acid or chromates, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with chromic acid or chromates should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substance from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic acid or chromates, the person performing the operation should be informed of chromic acid or chromates' hazardous properties.
- Where there is any possibility of exposure of an employee's body to solids or liquids containing chromic acid or chromates, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chromic acid or chromates should be removed immediately and not reworn until the substance is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing chromic acid or chromates contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solids or liquids containing chromic acid or chromates, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chromic acid or chromates should be immediately washed or showered with soap or mild detergent and water to remove any such sbustance.
- Workers subject to skin contact with solids or liquids containing chromic acid or chromates should wash with soap or mild detergent and water any areas of the body which may have contacted such a substance at the end of each work day.
- Eating and smoking should not be permitted in areas where solids or liquids containing chromic acid or chromates are handled, processed, or stored.
- Employees who handle solids or liquids containing chromic acid or chromates should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to a carcinogenic form of chromium (VI) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized personnel only.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromic acid or chromates may occur and control methods which may be effective in each case:

Operation	Controls
Use in metal finishing in chrome plating, anodizing, conversion coatings, and for corrossion resistance	Local exhaust ventilation; personal protective equipment
Use in leather finishing for shoe uppers, glove and garment leathers, and bag leather	Local exhaust ventilation; personal protective equipment
Use as corrosion inhibitors in radiator coolants, internal combustion and gas turbine engines, refrigerator and air conditioning systems, and water-cooled nuclear reactors	Local exhaust ventilation; personal protective equipment
Use in photoreproduction processes as sensitizing agents for photoengraving, photography, lithography, and blueprinting	Local exhaust ventilation; personal protective equipment

Operation	Controls
Use as corrosion-inhibiting and coloring pigments, artists' colors, jointing pastes, inks, rubber, and ceramics, and color blending	Process enclosure; local exhaust ventilation; personal protective equipment
Use in dyeing of fur, leather, fabrics, wool, and nylon; oxidizing of dyes; aftertreating on cotton, and in textile and paper printing; use in manufacture of glue used in shoes, furniture, and packaging	Local exhaust ventilation; personal protective equipment
Use as fungicides; use in aqueous preservatives and fire retardants for wood; for protection of textiles and seed	Local exhaust ventilation; personal protective equipment
Use in battery manufacture to increase shelf life; to provide corrosion resistance and for battery depolarization	Local exhaust ventilation; personal protective equipment
Use in manufacture of safety matches and explosives	Local exhaust ventilation; personal protective equipment
Use as a chemical reagent, oxidizing agent, catalyst, indicator, in bleaching of fats, oils, and waxes, in chemical synthesis, and in analytical chemistry	Local exhaust ventilation; personal protective equipment
Use in manufacture and packaging of cement	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solids or liquids containing chromic acid or chromates get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solids or liquids containing chromic acid get on the skin, immediately flush the contaminated skin with soap or mild detergent and water. If chromic acid soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If chromates get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing chromic acid or chromates penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chromic acid or chromates, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solids or liquids containing chromic acid or chromates have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If chromic acid or chromates are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromic acid or chromates should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Chromic acid or chromates may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

- **Warning properties**

RESPIRATORY PROTECTION FOR CHROMIC ACID AND CHROMATES

Condition	**Minimum Respiratory Protection*** **Required Above 0.1 mg/m³**
Particulate Concentration	
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
30 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 30 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Chromic and Chromous Salts (as Chromium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble chromic and chromous salts. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic sulfate hydrate

- Formula: $Cr_2(SO_4)_3\text{-}16H_2O$ (approximately)
- Synonyms: None
- Appearance and odor: Violet or green, odorless solid.

Chromic potassium sulfate

- Formula: $KCr(SO_4)_2\text{-}12H_2O$
- Synonyms: Potassium chrome alum; potassium chromium (III) sulfate
- Appearance and odor: Red-violet, odorless solid.

Chromous chloride

- Formula: $CrCl_2$
- Synonyms: None
- Appearance and odor: Colorless to gray, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble chromic or chromous salts is 0.5 milligrams of soluble chromic or chromous salts (as chromium) per cubic meter of air (mg/m³) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: They are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 mg/m³ and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/m³ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/m³ averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble chromic or chromous salts can affect the body if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Exposure to certain soluble chromic or chromous salts have been reported to cause an allergic skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble chromic or chromous salts.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble chromic and chromous salts at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble chromic and chromous salts exposure.

—Skin disease: Chromic salts may cause an allergic dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The soluble chromic and chromous salts have no established toxicity. Since exposures are often mixed, consideration should be given to the possible exposure to hexavalent chromium, which is a more toxic form. The compound hexaaquachromium trichloride has been found to react with protein in vitro, indicating that it is not biologically inert. Of 35 rats implanted with chromic acetate in the thigh muscle, 1 developed sarcoma; this was considered to be evidence of weak carcinogenicity of this soluble trivalent compound. When taken by mouth, the trivalent compounds do not give rise to local or systemic effects and are poorly absorbed; no specific effects are known to result from inhalation. Animals ingesting chromic salts showed one-ninth as much chromium in the tissues as did animals ingesting equal amounts of chromates. Dermatitis from some chromic salts has been reported. Some investigators believe that all persons sensitized to hexavalent chromium are also sensitive to the trivalent form, although this has not been firmly established.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Chromic sulfate hydrate**

1. Molecular weight: 680 (approximately)
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of chromic sulfate hydrate): Not applicable
5. Melting point: 90 C (194 F) Loses water, residue does not melt
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 84 – 120
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Chromic potassium sulfate**

1. Molecular weight: 499.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.83
4. Vapor density (air = 1 at boiling point of chromic potassium sulfate): Not applicable
5. Melting point: 89 C (192 F) Loses water, then melts at 400 C (752 F)
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 19.6
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Chromous chloride**

1. Molecular weight: 122.9
2. Boiling point (760 mm Hg): 1300 C (2372 F)
3. Specific gravity (water = 1): 2.93
4. Vapor density (air = 1 at boiling point of chromous chloride): Not applicable
5. Melting point: 820 C (1508 F)
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Water (chromyl chloride)
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Most soluble chromic or chromous salts are not combustible. However, chromyl chloride reacts vigorously with water, forming chromic acid, chromic chloride, hydrochloric acid, and chlorine. Also, chromyl chloride causes ignition of ammonia, ethyl alcohol, turpentine, and other combustible materials.

- **Warning properties**

Grant states that "chromium compounds . . . are known to cause dermatitis, ulcers of the skin and mucous membranes, and perforation of the nasal septum." Chromium chloride is an example of the chromium compounds which Grant states produces these effects. Not all chromic and chromous salts produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of soluble chromic or chromous salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of soluble chromic or chromous salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for soluble chromic and chromous salts is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquids or solids containing soluble chromic or chromous salts.
- Clothing contaminated with soluble chromic or chromous salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chromic or chromous salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic or chromous salts, the person performing the operation should be informed of soluble chromic or chromous salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with soluble chromic or chromous salts should be removed promptly and not reworn until the soluble chromic or chromous salts are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of liquids or solids containing soluble chromic or chromous salts contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquids or solids containing soluble chromic or chromous salts, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with soluble chromic or chromous salts should be promptly washed or showered to remove any soluble chromic or chromous salts.
- Employees who handle liquids or solids containing soluble chromic or chromous salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble chromic or chromous salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile treatment in dyeing, printing, moth-proofing, and water-proofing; use in tanning of leather in gloves, garments, and shoe uppers	Local exhaust ventilation; personal protective equipment
Use in manufacture of pigments for green varnishes, inks, paints, and glazes	Local exhaust ventilation; personal protective equipment
Use for metal treatment and polishing	Local exhaust ventilation; personal protective equipment
Use in photographic fixing baths for hardening of emulsions; use as catalysts and in manufacture of catalysts	Local exhaust ventilation; personal protective equipment
Use in chemical synthesis; use as corrosion inhibitors	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquids or solids containing soluble chromic or chromous salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If liquids or solids containing soluble chromic or chromous salts get on the skin, promptly flush the contaminated skin with water. If liquids or solids containing soluble chromic or chromous salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble chromic or chromous salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquids or solids containing soluble chromic or chromous salts have been swallowed give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble chromic or chromous salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble chromic or chromous salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble chromic or chromous salts may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

RESPIRATORY PROTECTION FOR SOLUBLE CHROMIC AND CHROMOUS SALTS (AS CHROMIUM)

Condition	**Minimum Respiratory Protection*** **Required Above 0.5 mg/m³**
Particulate Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume respirator or high efficiency particulate respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Chromium Metal and Insoluble Chromium Salts*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all chromium metal and insoluble chromium salts. Physical and chemical properties of some specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic chromium

- Formula: Cr
- Synonyms: None
- Appearance and odor: Shiny, odorless metal.

Copper chromite

- Formula: $Cu_2Cr_2O_4$
- Synonyms: Cuprous chromite
- Appearance and odor: Greenish-blue, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromium metal or insoluble chromium salts is 1 milligram of chromium metal or insoluble chromium salts per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 Cr (VI) mg/m^3 and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/m^3 averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chromium metal or insoluble chromium salts can affect the body if they are inhaled. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Ferro chrome alloys have been associated with lung changes in workers exposed to these alloys. Chromite dust exposure may cause minor lung changes.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chromium metal or insoluble chromium salts.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chromium metal or insoluble chromium salts at potentially hazardous levels:

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Chromium and its insoluble salts may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Insoluble chromium salts are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The dusts of chromium metal and its insoluble salts, chiefly the chromites, are usually reported to be relatively nontoxic; this is debatable, since exposures associated with toxic effects are usually mixed exposures involving several hexavalent chromium compounds. Ferrochrome alloys have been associated with pulmonary disease in humans. Four workers engaged in the production of ferrochrome alloys developed a nodular type of pulmonary disease with impairment of pulmonary function; air concentrations of chromium in this study averaged 0.26 mg/m^3, although other fumes and dusts were also present. This pulmonary problem may be one of hypersensitivity and thus reversible. Other reports state that chest roentgenograms have revealed only "exaggerated pulmonic markings" in workers exposed to chromite dust. The lungs of groups of workers exposed to chromite dust have been shown to be the seat of pneumoconiotic changes consisting of slight thickening of interstitial tissue and interalveolar septa, with histologic fibrosis and hyalinization. Chromite ore roast mixed with sheep fat implanted intrapleurally in rats produced squamous cell carcinomata coexisting with sarcomata of the lungs; the same material implanted in the thighs of rats produced fibrosarcomata. A refractory plant using chromite ore to make chromite brick had no excess of lung cancer deaths over a 14-year period, and it was concluded that chromite alone probably is not carcinogenic.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Metallic chromium**

1. Molecular weight: 52
2. Boiling point (760 mm Hg): 2640 C (4784 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of metallic chromium): Not applicable
5. Melting point: 1900 C (3452 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Copper chromite**

1. Molecular weight: 295.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 5.24
4. Vapor density (air = 1 at boiling point of copper chromite): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Basic potassium zinc chromate**

1. Molecular weight: 873.8
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 3.47
4. Vapor density (air = 1 at boiling point of basic potassium zinc chromate): Not applicable
5. Melting point: Loses water slowly above 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Chromium metal in contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None listed.
4. Special precautions: None listed.

- **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature (metal): 400 C (752 F) (layer); 580 C (1076 F) (cloud)
3. Minimum explosive dust concentration (metal): 230 grams/m^3
4. Extinguishant: Dry sand, dry dolomite, dry graphite

- **Warning properties**

Chromium metal and insoluble salts are not known to be eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chromium metal or insoluble chromium salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for chromium metal and insoluble chromium salts is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing insoluble chromium salts.
- Clothing contaminated with insoluble chromium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of insoluble chromium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the insoluble chromium salts, the person performing the operation should be informed of insoluble chromium salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with insoluble chromium salts should be removed promptly and not reworn until the insoluble chromium salts are removed from the clothing.
- Employees should be provided with and required to use dust- and splashproof safety goggles where solids or liquids containing insoluble chromium salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with insoluble chromium salts should be promptly washed or showered with soap or mild detergent and water to remove any insoluble chromium salts.
- Eating and smoking should not be permitted in areas where solids or liquids containing insoluble chromium salts are handled, processed, or stored.
- Employees who handle solids or liquids containing insoluble chromium salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromium metal or insoluble chromium salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in fabrication of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in preparation of alloy steels to enhance corrosion- and heat-resistance	Local exhaust ventilation; general dilution ventilation
Use in fabrication of plated products for decoration or increased wear-resistance	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of non-ferrous alloys to impart special qualities to the alloys	Local exhaust ventilation; general dilution ventilation
Use in production and processing of insoluble salts	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use as chemical intermediates; use in textile industry in dyeing, silk treating, printing, and moth-proofing wool	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in leather industry in tanning; use in photograhic fixing baths	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons	Local exhaust ventilation; general dilution ventilation
Use as fuel additives and propellant additives; in photogaphic fixing baths and in ceramics	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chromium metal or solids or liquids containing insoluble chromium salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solids or liquids containing insoluble chromium salts get on the skin, wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing insoluble chromium salts penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chromium metal or insoluble chromium salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solids or liquids containing insoluble chromium salts have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If chromium metal or insoluble chromium salts are spilled, the following steps should be taken:

1. Remove all ignition sources where metallic chromium has been spilled.
2. Ventilate area of spill.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromium metal or insoluble chromium salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Chromium metal or insoluble chromium salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chromium (as Cr)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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* SPECIAL NOTE

The International Agency for Research on Cance (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man,* Volume 2, 1973, and Volume 23, 1980

- **Method**

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on filter, followed by treatment with acid and atomic

RESPIRATORY PROTECTION FOR CHROMIUM METAL AND INSOLUBLE CHROMIUM SALTS (AS CHROMIUM)

Condition	**Minimum Respiratory Protection*** **Required Above 1 mg/m³**
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator.
10 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CLOPIDOL

INTRODUCTION

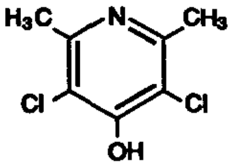
This guideline summarizes pertinent information about clopidol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_7Cl_2NO$

- **Structure**



- **Synonyms**

3,5-Dichloro-2,6-dimethyl-4-pyridinol; methylchloropindol; clopindol; Farmcoccid; Coccidiostat C; Coyden; Lerbek

- **Identifiers**

1. CAS No.: 2971-90-6
2. RTECS No.: UU7711500
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Clopidol is a white to light brown crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 192.06
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: Greater than 320°C (608°F)
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat. In cloud form, clopidol dust may explode if ignited.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving clopidol.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to clopidol; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving clopidol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving clopidol.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for clopidol is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure which should not be exceeded at any time during the workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned clopidol a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to clopidol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to clopidol can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Clopidol is an antibiotic used in veterinary medicine as a coccidiostat in poultry. This substance has a low order of acute and chronic toxicity in experimental animals [ACGIH 1991]. The oral LD_{50} in rabbits and guinea pigs is greater than 8 g/kg [NIOSH 1993]. The oral LD_{50} in rats is 18 g/kg [NIOSH 1993; Merck 1983]. Rats fed 15 mg/kg clopidol daily for 2 years showed no adverse effects [ACGIH 1991]. Dogs fed 5 mg/kg clopidol daily (duration of experiment not specified) also showed no adverse effects [ACGIH 1991].

2. *Effects on Humans:* In humans, exposure to clopidol dust may cause physical irritation of the eyes, nose, throat, and skin [NJDH 1986]. No chronic effects have been reported [NJDH 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to clopidol may cause redness and itching of the eyes, runny nose, sore throat, coughing, and redness and irritation of the skin.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to clopidol have been reported.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of clopidol is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve clopidol and may result in worker exposures to this substance:

—Manufacture and formulation of this substance

—Use as a coccidiostat in poultry

The following methods are effective in controlling worker exposures to clopidol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to toxic substances should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to clopidol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to clopidol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to clopidol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of clopidol on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for clopidol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne clopidol is determined by using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected (total dust) or with a 10-mm nylon cyclone preceding the glass fiber filter at a flow rate of 1.7 liter/min until a recommended air volume of 204 liters is collected (respirable fraction). Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If clopidol collects on the skin in excessive amounts, workers should wash the affected areas with soap and water.

Clothing excessively contaminated with clopidol should be removed to avoid local irritation of the skin.

A worker who handles clopidol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where clopidol or a solution containing clopidol is handled, processed, or stored.

STORAGE

Clopidol should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of clopidol should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving clopidol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or disposal.
4. Absorb liquid clopidol-containing formulations in vermiculite, dry sand, earth, or similar material.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Clopidol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of clopidol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of clopidol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although clopidol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of clopidol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only those respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent excessive skin contact with clopidol. Safety glasses, goggles, or face shields should be worn during operations in which clopidol might contact the eyes.

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Occupational Health Guideline for Coal Tar Pitch Volatiles

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

Anthracene

- Formula: $C_{14}H_{10}$
- Synonyms: None
- Appearance and odor: Pale green solid with a faint aromatic odor.

Phenanthrene

- Formula: $C_{14}H_{10}$
- Synonyms: None
- Appearance and odor: Colorless solid with a faint aromatic odor.

Pyrene

- Formula: $C_{16}H_{10}$
- Synonyms: None
- Appearance: Bright yellow solid

Carbazole

- Formula: $C_{12}H_9N$
- Synonyms: None
- Appearance and odor: Colorless solid with a faint aromatic odor.

Benzo(a)pyrene

- Formula: $C_{20}H_{12}$
- Synonyms: BaP, 3,4-benzopyrene
- Appearance and odor: Colorless solid with a faint aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for coal tar pitch volatiles is 0.2 milligram of coal tar pitch volatiles per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for coal tar products be reduced to 0.1 mg/m^3 (cyclohexane-extractable fraction) averaged over a work shift of up to 10 hours per day, 40 hours per week, and that coal tar products be regulated as occupational carcinogens. The NIOSH Criteria Document for Coal Tar Products and NIOSH Criteria Document for Coke Oven Emissions should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Coal tar pitch volatiles can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

Repeated exposure to coal tar pitch volatiles has been associated with an increased risk of developing bronchitis and cancer of the lungs, skin, bladder, and kidneys. Pregnant women may be especially susceptible to exposure effects associated with coal tar pitch volatiles. Repeated exposure to these materials may also cause sunlight to have a more severe effect on a person's skin. In addition, this type of exposure may cause an allergic skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to coal tar pitch volatiles.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to coal tar pitch volatiles at potentially hazardous levels:

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the oral cavity, respiratory tract, bladder, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders, for premalignant and malignant lesions, and evidence of hyperpigmentation or photosensitivity.

—Urinalysis: Coal tar pitch volatiles are associated with an excess of kidney and bladder cancer. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment, as well as a test for red blood cells.

—Urinary cytology: Coal tar pitch volatiles are associated with an excess of kidney and bladder cancer. Employees having 5 or more years of exposure or who are 45 years of age or older should have a urinary cytology examination.

—Sputum cytology: Coal tar pitch volatiles are associated with an excess of lung cancer. Employees having 10 or more years of exposure or who are 45 years of age or older should have a sputum cytology examination.

—14" x 17" chest roentgenogram: Coal tar pitch volatiles are associated with an excess of lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Coal tar pitch volatiles are reported to cause an excess of bronchitis. Periodic surveillance is indicated.

—A complete blood count: Due to the possibility of benzene exposure associated with coal tar pitch volatiles, a complete blood count is considered necessary to search for leukemia and aplastic anemia.

—Skin disease: Coal tar pitch volatiles are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, and semi-annually for employees 45 years of age or older or with 10 or more years' exposure to coal tar pitch volatiles.

- **Summary of toxicology**

Coal tar pitch volatiles (CTPV) are products of the destructive distillation of bituminous coal and contain polynuclear aromatic hydrocarbons (PNA's). These hydrocarbons sublime readily, thereby increasing the amounts of carcinogenic compounds in working areas. Epidemiologic evidence suggests that workers intimately exposed to the products of combustion or distillation of bituminous coal are at increased risk of cancer at many sites. These include cancer of the respiratory tract, kidney, bladder, and skin. In a study of coke oven workers, the level of exposure to CTPV and the length of time exposed were related to the development of cancer. Coke oven workers with the highest risk of cancer were those employed exclusively at topside jobs for 5 or more years, for whom the increased risk of dying from lung cancer was 10-fold; all coke oven workers had a 7-½-fold increase in risk of dying from kidney cancer. Although the causative agent or agents of the cancer in coke oven workers is unidentified, it is suspected that several PNA's in the CTPV generated during the coking process are involved. Certain industrial populations exposed to coal tar products have a demonstrated risk of skin cancer. Substances containing PNA's which may produce skin cancer also produce contact dermatitis; examples are coal tar, pitch, and cutting oils. Although allergic dermatitis is readily induced by PNA's in guinea pigs, it is only rarely reported in humans from occupational contact with PNA's; these have resulted largely from the therapeutic use of coal tar preparations. Components of pitch and coal tar produce cutaneous photosensitization; skin eruptions are usually limited to areas exposed to the sun or ultraviolet light. Most of the phototoxic agents will induce hypermelanosis of the skin; if chronic photodermatitis is severe and prolonged, leukoderma may occur. Some oils containing PNA's have been associated with changes of follicular and sebaceous glands which commonly take the form of acne. There is evidence that exposures to emissions at coke ovens and gas retorts may be associated with an increased occurrence of chronic bronchitis. Coal tar pitch volatiles may be associated with benzene, an agent suspected of causing leukemia and known to cause aplastic anemia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Anthracene**

1. Molecular weight: 178.2
2. Boiling point (760 mm Hg): 340 C (644 F)
3. Specific gravity (water = 1): 1.24
4. Vapor density (air = 1 at boiling point of anthracene): 6.15
5. Melting point: 217 C (423 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Phenanthrene**

1. Molecular weight: 178.2
2. Boiling point (760 mm Hg): 340 C (644 F)
3. Specific gravity (water = 1): 1.18
4. Vapor density (air = 1 at boiling point of phenanthrene): 6.15
5. Melting point: 100.5 C (213 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Pyrene**

1. Molecular weight: 202.3
2. Boiling point (760 mm Hg): Greater than 360 C (greater than 680 F)

3. Specific gravity (water = 1): 1.28
4. Vapor density (air = 1 at boiling point of pyrene): 6.9
5. Melting point: 150.4 C (303 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Carbazole**

1. Molecular weight: 167.2
2. Boiling point (760 mm Hg): 355 C (671 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of carbazole): 5.8
5. Melting point: 246 C (475 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Benzo(a)pyrene**

1. Molecular weight: 252.3
2. Boiling point (760 mm Hg): Greater than 360 C (greater than 680 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of benzo(a)pyrene): 8.7
5. Melting point: 179 C (354 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Flash point: Anthracene: 121 C (250 F) (closed cup); Others: Data not available
2. Autoignition temperature: Anthracene: 540 C (1004 F); Others: Data not available
3. Flammable limits in air, % by volume: Anthracene: Lower: 0.6; Others: Data not available
4. Extinguishant: Foam, dry chemical, and carbon dioxide

- **Warning properties**

Grant states that "coal tar and its various crude fractions appear principally to cause reddening and squamous eczema of the lid margins, with only small erosions of the corneal epithelium and superficial changes in the stroma, which disappear in a month following exposure. Chronic exposure of workmen to tar fumes and dust has been reported to cause conjunctivitis and discoloration of the cornea in the palpebral fissure, either near the limbus or, in extreme cases, across the whole cornea. Occasionally, epithelioma of the lid margin has been attributed to contact with coal tar."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Coal tar products may be sampled by collection on a glass fiber filter with subsequent ultrasonic extraction and weighing. An analytical method for coal tar pitch volatiles is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with condensed coal tar pitch volatiles, where skin contact may occur.
- If employees' clothing may have become contaminated with coal tar pitch volatiles, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with coal tar pitch volatiles

should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of coal tar pitch volatiles from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the coal tar pitch volatiles, the person performing the operation should be informed of coal tar pitch volatiles's hazardous properties.

- Employees should be provided with and required to use splash-proof safety goggles where condensed coal tar pitch volatiles may contact the eyes.

SANITATION

- Workers subject to skin contact with coal tar pitch volatiles should wash with soap or mild detergent and water any areas of the body which may have contacted coal tar pitch volatiles at the end of each work day.
- Employees who handle coal tar pitch volatiles should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to coal tar pitch volatiles may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to coal tar pitch volatiles may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from extraction and packaging from coal tar fraction of coking	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a binding agent in manufacture of coal briquettes used for fuel; use as a dielectric in the manufacture of battery electrodes, electric-arc furnace electrodes, and electrodes for alumina reduction	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of roofing felts and papers and roofing	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use for protective coatings for pipes for underground conduits and drainage; use as a coating on concrete as waterproofing and corrosion-resistant material; use in road paving and sealing	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture and repair of refractory brick; use in production of foundry cores; use in manufacture of carbon ceramic items	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If condensed coal tar pitch volatiles get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If condensed coal tar pitch volatiles get on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands before eating or smoking and to wash thoroughly at the close of work.

- **Breathing**

If a person breathes in large amounts of coal tar pitch volatiles, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If coal tar pitch volatiles are released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of spill.

2. Collect released material in the most convenient and safe manner for reclamation or for disposal in sealed containers in a secured sanitary landfill.

- Waste disposal method:

Coal tar pitch volatiles may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR COAL TAR PITCH VOLATILES

Condition	**Minimum Respiratory Protection*** **Required Above 0.2 mg/m³**
Particulate and Vapor Concentration	
2 mg/m³ or less	A chemical cartridge respirator with an organic vapor cartridge(s) and with a fume or high-efficiency filter. Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m³ or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s) and with a fume or high-efficiency filter. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and with a full facepiece and a fume or high-efficiency filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode. A powered air-purifying respirator with an organic vapor cartridge and a high-efficiency particulate filter.
400 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 400 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Cobalt Metal Fume and Dust

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formulas of example compounds: $Co/CoO/Co_2O_3/Co_3O_4$
- Synonyms: None
- Appearance and odor: Odorless black solid or finely divided particulate dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cobalt metal fume and dust is 0.1 milligram of cobalt metal fume and dust per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for cobalt metal fume and dust a Threshold Limit Value of 0.05 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cobalt metal fume and dust can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Cobalt metal fume and dust cause irritation of the nose and throat. They have also been reported to cause respiratory disease with symptoms ranging from cough and shortness of breath to permanent disability and death. The symptoms frequently go away when exposure is stopped, but sometimes the symptoms progress after exposure has ceased. Exposure to cobalt may cause an allergic skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cobalt metal fume and dust.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cobalt metal fume and dust at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Cobalt may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Cobalt is reported to decrease pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Cobalt metal fume and dust cause upper respiratory tract irritation, chronic interstitial pneumonitis, and skin sensitization. Rhabdomyosarcomata developed in rats injected intramuscularly with the powder of either pure cobalt metal or cobalt oxide. Animals were exposed to the repeated inhalation of the cobalt metal blend used by the cemented carbide industry: a concentration of 20 mg/m^3 of cobalt for 3 years produced hyperplasia of the bronchial epithelium and focal fibrotic lesions of the lungs with developing granulomata; daily inhalation of cobalt metal fume composed of approximately equal parts of cobalt, cobalt oxide, and cobaltic-cobaltous

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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oxide did not elicit these reactions. Guinea pigs developed acute pneumonitis, often rapidly fatal, from the intratracheal injection of cobalt metal or repeated inhalation of a mixture of 75% tungsten carbide and 25% cobalt. Chronic interstitial pneumonitis has been reported in workers in the cemented carbide industry, and cobalt has been conditionally implicated as the etiologic agent by a process of elimination of the other materials used in the industry. Symptoms range from shortness of breath, cough, and dyspnea on exertion to permanent disability or death in some cases. Among 12 workers exposed to cobalt engaged in manufacture of, or grinding with, tungsten carbide tools, who developed interstitial lung disease, there were 8 fatalities; serial chest roentgenograms over a period of 3 to 12 years revealed gradually progressive densities of a linear and nodular nature which gradually involved major portions of both lungs; cough, dyspnea on exertion, and reduced pulmonary function occurred early in the course of the disease. The disease has features of hypersensitivity; only a small percentage of people exposed are affected and with little evidence of dose-response relationship. Cobalt and its compounds produce an allergic dermatitis of an erythematous papular type, which usually occurs in skin areas subjected to friction, such as the ankles, elbow flexures, and sides of the neck.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 58.93 to 181.9
  2. Boiling point (760 mm Hg): 3100 C (5612 F)
  3. Specific gravity (water = 1): 8.8
  4. Vapor density (air = 1 at boiling point of cobalt metal fume and dust): Not applicable
  5. Melting point: 1491 C (2715 F)
  6. Vapor pressure at 20 C (68 F): 0 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact of dust with strong oxidizers may cause fire and explosions.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Flash point: Not applicable
  2. Autoignition temperature: Specially prepared (the form prepared by reducing the oxides in hydrogen) very fine cobalt dust will catch fire at room temperature in air.
  3. Flammable limits in air, % by volume: Not applicable
  4. Extinguishant: Dry sand, dry dolomite, dry graphite powder
- **Warning properties**

The AIHA *Hygienic Guide* states that "cobalt appears to be an eye irritant. One of the findings in the study of the tungsten carbide industry was a significant amount of conjunctivitis, presumably caused by the cobalt used as 'cement'." Contact with industry has indicated that workers in the cobalt-cemented tungsten industry have not experienced eye irritation to cobalt below 1 mg/m^3.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cobalt metal fume and dust on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for cobalt metal fume and dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with cobalt dust.

- If employees' clothing may have become contaminated with cobalt dust, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with cobalt dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cobalt dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cobalt dust, the person performing the operation should be informed of cobalt dust's hazardous properties.
- Non-impervious clothing which becomes contaminated with cobalt dust should be removed promptly and not reworn until the cobalt dust is removed from the clothing.

SANITATION

- Skin that becomes contaminated with cobalt dust should be promptly washed or showered with soap or mild detergent and water to remove any cobalt dust.
- Eating and smoking should not be permitted in areas where cobalt metal fume or dust are generated, handled, processed, or stored.
- Employees who handle cobalt metal fume or dust should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cobalt metal fume and dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use as a binder in manufacture of cemented carbide items; during refining and concentration of ores; during preparation of alloys	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of metal items from magnetic alloy; during manufacture of metal items from super- and high-temperature alloys	Local exhaust ventilation; personal protective equipment
Liberation during grinding and sharpening of cemented carbide and steel tools; during synthesis of cobalt compounds for use as pigments and as catalysts and driers; during refining and concentrations of ores	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of metal items from cutting tool and tool steels; during manufacture of metal items from hard-facing alloys; during manufacture of items containing low-expansion alloys; during manufacture of metal items containing constant-modulus alloys; metal to glass seals in electric lamps, vacuum tubes, and x-ray tubes	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of dental prosthetic and osteosynthetic items; during asbestos fiber processing	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cobalt metal dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If cobalt metal fume or dust get on the skin, wash the contaminated skin using soap or mild detergent and water. If cobalt metal dust penetrates through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of cobalt metal fume or dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When cobalt metal dust has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If cobalt dust is spilled or if potentially hazardous amounts of cobalt metal fume are inadvertently released, the following steps should be taken:

1. Ventilate area of spill.
2. Collect released material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Cobalt dust may be placed in sealed containers and disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR COBALT METAL FUME AND DUST

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1.0 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT CARBONYL

INTRODUCTION

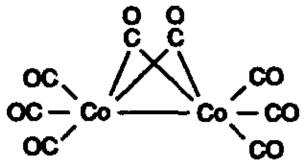
This guideline summarizes pertinent information about cobalt carbonyl (measured as Co) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8Co_2O_8$

- **Structure**



- **Synonyms**

Cobalt octacarbonyl, cobalt tetracarbonyl, cobalt tetracarbonyl dimer, di-μ-carbonylhexacarbonyl-dicobalt, dicobalt carbonyl, dicobalt octacarbonyl, octacarbonyldicobalt

- **Identifiers**

1. CAS No.: 10210-68-1
2. RTECS No.: GG0300000
3. DOT UN: 9188 31 (Hazardous substance, liquid, or solid, n.o.s.)
4. DOT label: None

- **Appearance and odor**

Cobalt carbonyl is an orange to dark brown crystalline solid, although the pure substance is white.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 341.94
2. Boiling point (at 760 mm Hg): Decomposes at temperatures above 52°C (125.6°F)
3. Specific gravity (water = 1): 1.87 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 51°C (123.8°F)
6. Vapor pressure at 15°C (59°F): 0.07 mm Hg
7. Solubility: Insoluble in water; soluble in alcohol, ether, naphtha, and carbon disulfide
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Exposure of cobalt carbonyl to air or heat causes decomposition to occur. Cobalt carbonyl is slowly attacked by sulfuric

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acid or hydrochloric acid and is more rapidly attacked by bromine and nitric acid.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) and the pyrophoric dodecacarbonyltetracobalt may be released in a fire involving cobalt carbonyl.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to cobalt carbonyl.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Data not available

4. Extinguishant: For small fires involving cobalt carbonyl, use dry chemical, carbon dioxide, water spray, or standard foam. For large fires, use water spray, fog, or standard foam.

Fires involving cobalt carbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Containers of cobalt carbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Do not scatter this material with high-pressure water streams. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt carbonyl. Structural firefighters' protective clothing may provide limited protection against fires involving this substance.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt carbonyl (measured as Co) [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt carbonyl (measured as Co) a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation. The ACGIH limit is based on the risk of pulmonary and other acute effects associated with exposure to cobalt carbonyl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cobalt carbonyl can occur through inhalation, ingestion, and contact with the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cobalt carbonyl damages the respiratory and central nervous systems, liver, and kidneys, and may also irritate and sensitize the skin of animals on contact. Administered topically or subcutaneously to rats and mice, cobalt carbonyl was absorbed through the skin in toxic amounts and caused irritation of the skin [NLM 1990]. Applied to the skin of guinea pigs, cobalt carbonyl caused an allergic reaction [NLM 1990]. The LC$_{50}$ (duration unspecified) in rats is 165 mg/m^3 [NIOSH 1989] and the 2-hr LC$_{50}$ in mice is 27 mg/m^3 [Sax and Lewis 1989]. Rats exposed to concentrations of cobalt carbonyl ranging from 8 to 44 mg/m^3 for 30 min showed inflammatory and proliferative changes in the lungs at autopsy; at the highest concentrations, there was evidence of pulmonary edema. Histopathological changes and adverse effects on the central nervous system, liver, and kidneys were seen at autopsy; decreased thyroid function was also observed in these animals [NLM 1990]. The oral LD$_{50}$ is 754 mg/kg in

rats [NIOSH 1989] and 378 mg/kg in mice [Sax and Lewis 1989].

2. *Effects on Humans:* Cobalt carbonyl causes sensory irritation on contact with the skin and mucous membranes [Parmeggiani 1983], and affects the respiratory system and the blood. Factory workers acutely overexposed to airborne cobalt carbonyl developed bronchospasm, showed X-ray evidence of focal infiltrations of the lungs, and had changes in several cellular blood components [NLM 1990]. Based on the toxicologic similarities between nickel carbonyl and cobalt carbonyl, it is likely that overexposure to cobalt carbonyl would give rise to nausea, headache, dizziness, coughing, dyspnea, and substernal pain [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cobalt carbonyl may cause cough, shortness of breath, lung densities, decreased pulmonary function, wheezing, and pain in the chest. Clinical evidence of changes in the cellular components of the blood may also be present. Ingestion could cause pericardial effusion, pain, vomiting, nerve deafness, convulsions, and thyroid enlargement.

2. *Chronic exposure:* Continued low-level exposure to cobalt carbonyl may cause cough, rapid breathing on exertion, decreased pulmonary function, wheezing, and shortness of breath.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cobalt carbonyl or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do not give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt carbonyl and result in worker exposures to this substance:

—Use as a catalyst for organic reactions

—Use as a catalyst in the plastics industry

—Preparation of metals of high purity

The following methods are effective in controlling worker exposures to cobalt carbonyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cobalt carbonyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory and nervous systems, liver, kidneys, and blood. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt carbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or nervous system, liver, kidneys, or blood.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt carbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt carbonyl on the respiratory or nervous system, liver, kidneys, or blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt carbonyl.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to cobalt carbonyl may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt carbonyl (measured as cobalt) is determined by using a 0.8 micron mixed cellulose ester filter. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Computerized Information System [OSHA 1990], the *OSHA Analytical Methods Manual* [OSHA 1985], the *OSHA Chemical Information Manual* [OSHA 1987], and in Method 7027 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If cobalt carbonyl contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min, and then wash with soap and water.

Clothing contaminated with cobalt carbonyl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cobalt carbonyl, particularly its potential to cause headache, nausea, and pulmonary effects.

A worker who handles cobalt carbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt carbonyl or a solution containing this substance is handled, processed, or stored.

STORAGE

Cobalt carbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt carbonyl should be protected from physical damage and should be stored separately from hydrochloric acid, sulfuric acid, nitric acid, bromine, heat, sparks, and open flame. Because containers that formerly contained cobalt carbonyl may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cobalt carbonyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Cover the spill area with a plastic sheet or tarp to minimize spreading.
2. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of cobalt carbonyl must comply with EPA's emergency planning requirements [40 CFR Part 355.30]. (If cobalt carbonyl is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of cobalt carbonyl are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for cobalt carbonyl is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt carbonyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt carbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt carbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt carbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt carbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt carbonyl.

If cobalt carbonyl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt carbonyl might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt carbonyl. Contact lenses should not be worn if the potential exists for cobalt carbonyl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT HYDROCARBONYL

INTRODUCTION

This guideline summarizes pertinent information about cobalt hydrocarbonyl (measured as cobalt) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$HCo(CO)_4$

- **Synonyms**

Tetracarbonylhydrocobalt; hydridotetracarbonyl cobalt; hydrocobalt tetracarbonyl; tetracarbonylhydridocobalt

- **Identifiers**

1. CAS No.: 16842-03-8
2. RTECS No.: GG0900000
3. DOT UN: 1954 22 (Flammable gas, n.o.s.)
4. DOT label: Flammable gas

- **Appearance and odor**

Cobalt hydrocarbonyl is a flammable gas that is unstable and decomposes rapidly at room temperature.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 171.98
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity: Data not available
4. Relative gas density: 5.93
5. Freezing point: -26.2°C (-15.2°F)
6. Vapor pressure at 20°C (68°F): >1 atm
7. Solubility: Sparingly soluble in water
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Contact of cobalt hydrocarbonyl with air causes decomposition.
2. Incompatibilities: None reported
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving cobalt hydrocarbonyl.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for cobalt hydrocarbonyl; however, this substance is flammable.

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National Institute for Occupational Safety and Health
Education and Information Division

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Occupational Safety and Health Administration

1. Flash point: Not applicable (Flammable gas)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical or carbon dioxide for small fires and water spray or fog for large fires.

Fires involving cobalt hydrocarbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cobalt hydrocarbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions, and let the tank car or truck burn unless the leak can be stopped. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt hydrocarbonyl. Structural firefighters' protective clothing will provide limited protection.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt hydrocarbonyl [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt hydrocarbonyl a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation associated with exposure to cobalt hydrocarbonyl. The ACGIH limit is based on the risk of lung, liver, and kidney effects associated with exposure to cobalt hydrocarbonyl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cobalt hydrocarbonyl can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cobalt hydrocarbonyl affects the respiratory system. The 2-hr LC$_{50}$ for cobalt hydrocarbonyl is 46.2 mg/m^3 in rats and 17.5 mg/m^3 in mice [NIOSH 1993]. Acutely poisoned animals showed signs of chemical pneumonitis before death [Palmer et al. 1959]. Dogs, rats, and guinea pigs exposed 6-hr/day on 71 occasions within a 3-month period to cobalt hydrocarbonyl decomposition products at an average cobalt concentration of 9 mg/m^3 showed elevated hemoglobin levels (rats) and foam cell aggregates in the lungs; these signs disappeared after the cessation of exposure [Palmer et al. 1959].

2. *Effects on Humans:* No adverse effects of exposure to cobalt hydrocarbonyl have been reported in humans.

- **Signs and symptoms of exposure**

1. *Acute or sub-chronic exposure:* Based on effects seen in animals, subchronic exposure to cobalt hydrocarbonyl may cause difficult breathing, coughing, reduced lung function, and fluid in the lungs.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to cobalt hydrocarbonyl have been reported.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt hydrocarbonyl and may result in worker exposures to this substance:

—Manufacture of cobalt hydrocarbonyl

—Use as a catalyst

The following are methods that are effective in controlling worker exposures to cobalt hydrocarbonyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cobalt hydrocarbonyl, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt hydrocarbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt hydrocarbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt hydrocarbonyl on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt hydrocarbonyl.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt hydrocarbonyl (measured as cobalt) is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a recommended flow rate of 2.0 liters/min until a recommended air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy for total cobalt. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cobalt hydrocarbonyl contacts the skin, the victim should immediately and thoroughly wash the affected areas with soap and water.

Clothing contaminated with cobalt should be removed immediately.

A worker who is exposed to cobalt hydrocarbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt hydrocarbonyl is generated.

STORAGE

Cobalt hydrocarbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt hydrocarbonyl should be protected from physical damage and should be stored separately from air, heat, sparks, and open flame.

LEAKS

In the event of a leak involving cobalt hydrocarbonyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a leak:

1. Notify safety personnel.

2. Remove all sources of heat and ignition.

3. Ventilate potentially explosive atmospheres.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cobalt hydrocarbonyl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cobalt hydrocarbonyl; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt hydrocarbonyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt hydrocarbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt hydrocarbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt hydrocarbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt hydrocarbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt hydrocarbonyl.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt hydrocarbonyl might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt hydrocarbonyl.

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Occupational Health Guideline for Copper Dusts and Mists

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formulas of example compounds: $CuSO_4$-$5H_2O$; CuCl
- Example compounds: Copper sulfate dust or mist; cuprous chloride dust
- Appearance and odor: Odorless solids

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for copper dusts or mists is 1 milligram of copper dusts or mists per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Copper dusts or mists can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Powdered copper or dusts or mists of copper salts may cause a feeling of illness similar to the common cold with sensations of chills and stuffiness of the head. Small copper particles may enter the eye and cause irritation, discoloration, and damage.

2. Long-term Exposure: Repeated or prolonged exposure to copper dusts or mists may cause skin irritation or discoloration of the skin or hair.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to copper dusts or mists.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to copper dusts and mists at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from copper dusts and mists exposure.

—Chronic respiratory disease: Copper dusts or mists cause respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper dusts or mists might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Copper dusts or mists cause liver damage in animals. Persons with pre-existing liver disease may be more susceptible to the effects of these agents.

—Kidney disease: Copper dusts or mists cause kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Skin sensitization in human subjects has occurred. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

—Hematopoietic disorders: Anemia has occurred in animals given copper salts orally. Persons with pre-existing blood disorders may be more susceptible to the effects of these agents.

—Wilson's disease: Persons with pre-existing Wilson's disease may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Inhalation of dusts and mists of copper and copper salts results in irritation of the upper respiratory tract, with occasional ulceration and perforation of the nasal septum. Inhalation of copper and its compounds by animals caused injury to the lungs and liver with

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hemochromatosis. Access of sheep to salt licks containing 5 to 9% copper sulfate caused the sudden onset of hemolytic anemia, icterus, and hemoglobinuria followed by death in a day or two; at necropsy, the liver, kidneys, and spleen showed severe degenerative changes. Workers exposed to copper dust in concentrations of 0.075 to 0.120 mg/m^3 complained of mild nasal discomfort. Exposure to the dust of copper acetate produced sneezing, coughing, digestive disorders, and fever. Metal workers exposed to complex copper salts in dust form complained of metallic taste with irritation of nasal and oral mucosa; atrophic changes in the mucous membranes were noted in subjects exposed for long periods of time. On ingestion, copper salts act as irritants and cause nausea, vomiting, abdominal pain, hemorrhagic gastritis, and diarrhea. Copper salts splashed in the eye cause conjunctivitis, corneal ulceration, and turbidity, and may produce palpebral edema. Copper particles embedded in the eye result in pronounced foreign-body reaction with characteristic discoloration of ocular tissue. Allergic contact dermatitis due to copper exposure, although rare, has been reported. Greenish discoloration of the skin and hair of some copper workers has been observed. Although copper is an essential element for health, excessive amounts can produce harmful effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: $CuSO_4$: 249.7; $CuCl_2$: 99
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of copper dusts or mists): Not applicable
5. Melting point: Higher than 100 C (212 F). For example, copper sulfate = 150 C (302 F); cuprous chloride = 430 C (806 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): Ranges from very low (e.g. cuprous chloride = 0.006) to high (e.g. copper sulfate = 35)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Extreme heat
2. Incompatibilities: Copper dusts or mists may react with acetylene gas to form copper acetylides, which are solids that are sensitive to shock. Some copper mists may react with magnesium metal to form flammable hydrogen gas.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Ignition temperature: Copper dusts = 700 C (1292 F)

- **Warning properties**

According to Grant, copper acetoarsenite, copper chloride, copper sulfate, copper carbonate and oxide, and copper metal all produce local irritant effects when in contact with the eye. The *Documentation of TLV's* also notes that copper salts on the eye may cause "conjunctivitis or even ulceration and turbidity of the cornea." Concentrations producing these effects are not given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of copper dusts or mists on a cellulose ester membrane filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for copper dusts or mists is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with copper salts or liquids containing copper salts.

- If employees' clothing may have become contaminated with powdered copper, copper salts, or liquids containing copper salts, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with copper salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of copper salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the copper salts, the person performing the operation should be informed of copper salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with copper salts should be removed promptly and not reworn until the copper salts are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where powdered copper or dusts, mists, or liquids containing copper salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with copper salts should be promptly washed or showered with soap or mild detergent and water to remove any copper salts.
- Eating and smoking should not be permitted in areas where powdered copper, copper salts, or liquids containing copper salts are handled, processed, or stored.
- Employees who handle powdered copper, copper salts, or liquids containing copper salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to copper dusts or mists may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining, extracting, and refining copper ore; during fabrication and manufacture of copper rod, wire, piping, and tubing for use in electrical, plumbing, and building industries; during manufacture of domestic utensils; during manufacture of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from production and application of fungicides, insecticides, and germicides for soil, feed, grain, textile, water and sewage treatments; during use of copper salts for paint pigments and coloring agents, electroplating baths, wood preservation, automotive emission controls, textile treatment, and organic synthesis	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If copper dusts or mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If copper salts or liquids containing copper salts get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If copper salts or liquids containing copper salts penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of copper dusts or mists, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When powdered copper, copper salts, or liquids containing copper salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of release until cleanup has been completed.
- If copper dusts or mists are spilled or released, the following steps should be taken:

1. Ventilate area of release.
2. Collect spilled material in the most convenient and safe manner for reclamation, or for disposal in a secured sanitary landfill. Liquid containing copper should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Copper dusts or mists and copper compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Copper as Cu," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR COPPER DUSTS AND MISTS

Condition	**Minimum Respiratory Protection* Required Above 1 mg/m³**
Particulate Concentration	
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Copper Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cu/Cu_2O/CuO$
- Synonyms: None
- Appearance: Finely divided particulate dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for copper fume is 0.1 milligram of copper fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for copper fume a Threshold Limit Value of 0.2 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Copper fume can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Copper fume causes irritation of the eyes, nose, and throat, and a flu-like illness called metal fume fever. Symptoms of metal fume fever include fever, muscle aches, nausea, chills, dry throat, cough, and weakness. It may also cause a metallic or sweet taste in the mouth.

2. Long-term Exposure: Repeated or prolonged exposure to copper fume may cause the skin and hair to change color.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to copper fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to copper fume at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from copper fume exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper fume might cause exacerbation of symptoms due to its irritant properties.

—Hepatolenticular degeneration (Wilson's disease): Persons with pre-existing Wilson's disease may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Inhalation of copper fume results in irritation of the upper respiratory tract and an influenza-like illness termed metal fume fever. Signs and symptoms of metal fume fever include chills, muscle aches, nausea, fever, dry throat, cough, weakness, and lassitude. There is usually leucocytosis, which may amount to 12,000 to 16,000/ml; recovery is usually rapid, and there are no sequelae. Most workers develop an immunity to these attacks, but it is quickly lost; attacks tend to be more severe on the first day of the work-week. Other effects from copper fume are irritation of the upper respiratory tract, metallic or sweet taste, and in some instances discoloration of the skin and hair. Exposure of workers to concentrations of 1 to 3 mg/m^3 for short periods resulted in altered taste response but no nausea; levels of from 0.02 to 0.4 mg/m^3 produced no complaints. Transient irritation of the eyes has followed exposure to a

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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fine dust of oxidation products of copper produced in an electric arc.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 63.5 to 143.1
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): Not applicable
  4. Vapor density (air = 1 at boiling point of copper fume): Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with acetylene gas may cause formation of copper acetylides that are sensitive to shock.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not applicable
- **Warning properties**

Copper fume is not known to be a significant eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of copper fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for copper fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to copper fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during construction and installation of materials fabricated from copper metal or copper alloys; during copper metal processing of castings, sheets, rods, tubing, and wire; during copper metal smelting and refining operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of copper fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of copper fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Copper as Cu," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR COPPER FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COTTON DUST

INTRODUCTION

This guideline summarizes pertinent information about cotton dust for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

"Cotton dust" is defined as dust generated into the atmosphere as a result of the processing of cotton fibers combined with any naturally occurring materials such as stems, leaves, bracts, and inorganic matter which may have accumulated on the cotton fibers during the growing or harvesting period. Any dust generated from the processing of cotton through the weaving of fabric in textile mills and dust generated in other operations or manufacturing processes using new or waste cotton fibers or cotton fiber by-products from textile mills is also considered cotton dust.

SUBSTANCE IDENTIFICATION

- **Identifiers:** RTECS GN2275000; DOT 1365 (cotton, wet or contaminated), label required: "Spontaneously Combustible"
- **Appearance:** Whitish solid (fibers and/or particulates)

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Specific gravity (water = 1): 1.3 (approximate)
2. Insoluble in water

- **Reactivity**

Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

- **Flammability**

1. Minimum ignition temperature: 470°C (878°F), cotton flock
2. Minimum explosive dust concentration: 0.05 g/L (50 g/m^3), cotton flock
3. Extinguishant: Water
4. Combustible solid (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, cotton dust should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cotton dust is 200 micrograms of cotton dust per cubic meter of air ($\mu g/m^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift in yarn manufacturing and cotton washing operations; 750 $\mu g/m^3$ as a TWA over an 8-hour workshift in textile slashing and weaving operations; and 500 $\mu g/m^3$ as a TWA over an 8-hour workshift in textile mill waste house operations and dust from lower grade washed cotton in yarn manuacturing; and 1,000 $\mu g/m^3$ as a TWA over an 8-hour workshift in cotton waste processing operations of waste recycling (sorting, blending, cleaning, willowing, and garnetting). The National Institute for Occupational Safety and Health (NIOSH) recommends that exposure to cotton dust be reduced to the lowest feasible limit, which is defined as being a recommended exposure limit (REL) of less than 200 $\mu g/m^3$. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for cotton dust (raw) is 200 $\mu g/m^3$ as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cotton dust

	Exposure limits $\mu g/m^3$
OSHA PEL TWA	200 (yarn manufacturing and cotton washing)
	750 (slashing and weaving)
	500 (textile mill waste house operations and lower grade washed cotton in yarn manufacturing)
	1,000 (waste recycling and garnetting)
NIOSH REL	<200
ACGIH TLV TWA	200

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Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cotton dust may cause adverse health effects following exposure via inhalation.

- **Summary of toxicology**

1. *Effects on animals:* In rabbits, inhalation of cotton dust combined with bacterial *(Escherichia coli)* endotoxin caused bronchitis.
2. *Effects on humans:* Short-term exposure to cotton dust has caused bronchitis and acute byssinosis (also known as "Brown Lung" or "Monday Morning Fever"), a reversible respiratory disease produced by inhalation of cotton dust. Chronic exposure has caused lung airway obstruction (which reduces ventilatory capacity) and has led to disability and premature death. A direct relationship has been observed between the total concentration of cotton dust exposure and the rate of development of byssinosis. Among workers exposed to cotton dust, cigarette smokers have an increased risk of developing byssinosis. The biologically active material in cotton dust has not been ascertained; however, the risk of developing byssinosis appears to be reduced for workers who are exposed to dust from washed cotton.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cotton dust can produce a feeling of chest tightness, coughing, wheezing, phlegm, weakness, fever, chills, and breathing difficulty (dyspnea). These symptoms can disappear following removal from exposure (during brief periods away from work) and can reappear following reexposure.
2. *Long-term (chronic):* Exposure to cotton dust can cause permanent and disabling breathing difficulties that include chronic bronchitis with emphysema.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to cotton dust should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cotton dust, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cotton dust at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to cotton dust. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, pre- and post-shift tests of lung function, and chest X-rays.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cotton dust may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events
1. Acute SHE's include: Byssinosis (acute form)
2. Delayed-onset SHE's include: Byssinosis (chronic form) and chronic bronchitis with emphysema

MONITORING AND MEASUREMENT PROCEDURES

• Method
Sampling and analysis may be performed by collecting cotton dust using a vertical elutriator preselector with a high-efficiency membrane filter and analyzing by gravimetric methods. Detailed sampling and analytical methods for cotton dust may be found in the *Criteria for a Recommended Standard. . . .Occupational Exposure to Cotton Dust.*

SANITATION

Cleaning of equipment by "blowing-down" with compressed air or dry sweeping should be avoided. Vacuum cleaning should be instituted for all processes whenever possible. If "blow-down" is necessary, it should be conducted only in the absence of personnel not directly involved in the "blow-down" operation. Those workers involved in "blow-down" should wear adequate respiratory protection.

Good housekeeping practices designed to prevent the re-suspension of settled dust shall be developed and followed at all times.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cotton dust should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cotton dust may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cotton dust

Operations	Controls
During carding operations, mixing and blowing opertions, bale breaking, manufacturing of cotton yarn, and handling of cottonseed in the extraction of cottonseed oil	Process enclosure, local exhaust ventilation, personal protective equipment
During cotton batting operations and weaving of textiles containing cotton yarn	General dilution ventilation
During raw cotton ginning, bale pressing, and harvesting	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

• Eye exposure
Where there is any possibility of a worker's eyes being exposed to cotton dust, an eye-wash fountain should be provided within the immediate work area for emergency use. Contact lenses should not be worn when working with this substance.

SPILLS AND LEAKS

In cases in which environmental levels exceed the NIOSH REL, workers not wearing respiratory protection should be restricted from areas of cotton dust contamination until cleanup has been completed.

If cotton dust contamination occurs, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of contamination.
3. Cotton dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container. If a vacuum system is used, there should be no sources of ignition in the vicinity of the contamination, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cotton dust

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 $\mu g/m^3$	Any dust respirator
Less than or equal to 2,000 $\mu g/m^3$	Any dust respirator except single-use and quarter-mask respirators Any supplied-air respirator Any air-purifying respirator with a high-efficiency particulate filter Any self-contained breathing apparatus
Less than or equal to 5,000 $\mu g/m^3$	Any powered air-purifying respirator with a dust filter Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 10,000 $\mu g/m^3$	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Planned or emergency entry into environments containing unknown concentrations or levels above 10,000 $\mu g/m^3$	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

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*Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of $<200\ \mu g/m^3$.

Occupational Health Guideline for Crag Herbicide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $2,4\text{-}Cl_2C_6H_3OC_2H_{4G1}{}^{OSO}{}_3Na$
- Synonyms: Sesone; Crag herbicide No. 1; sodium 2-(2,4-dichlorophenoxy)ethyl sulfate
- Appearance and odor: Colorless solid with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Crag herbicide is 15 milligrams of Crag herbicide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for Crag herbicide a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Crag herbicide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Animal experiments have shown that exposure to Crag herbicide may cause tremors, muscle spasms, and convulsions. It has also caused congestion of the lungs, liver, and kidneys in animals. A solution of Crag herbicide dropped in animal eyes caused damage. The solution applied to animal skin has caused skin irritation and damage.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Crag herbicide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Crag herbicide at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from Crag herbicide exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Crag herbicide might cause exacerbation of symptoms since it causes pulmonary hemorrhage in animals at lethal doses.

—Liver disease: Crag herbicide causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Crag herbicide causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Crag herbicide is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Convulsive disorders: Crag herbicide (Sesone) causes convulsions in animals. Persons with a history of such disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Crag herbicide (Sesone) dust affects the nervous system in animals and causes convulsions. In rats the oral LD50 ranged from 0.73 to 1.09 g/kg; effects were a fine

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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muscular tremor, myotonus, a tendency to extend the hind feet caudally, and convulsions. Autopsy findings in animals that died were pulmonary hemorrhage, with mild liver and kidney damage. A 5% aqueous solution dropped in the eye of a rabbit caused corneal necrosis. The application of 0.01 ml of a 5% suspension of Sesone in acetone to the shaved rabbit belly resulted in edema and necrosis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 309
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of Crag herbicide): Not applicable
5. Melting point: 170 C (338 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 25
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, sulfur dioxide, and carbon monoxide) may be released when Crag herbicide decomposes.
4. Special precautions: None.

- **Flammability**

1. Not combustible.

- **Warning properties**

Union Carbide Corporation, in the *Chemical Company Guide* for Crag herbicide, states that "flooding the rabbit eye with a saturated solution of the chemical in propylene glycol caused a reaction similar to moderate inflammation. The dry powder can be expected to have an additional mechanical irritant action."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for Crag herbicide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with Crag herbicide or liquids containing Crag herbicide.
- If employees' clothing may have become contaminated with Crag herbicide or liquids containing Crag herbicide, employees should change into uncontaminated clothing before leaving the work premises.
- Non-impervious clothing which becomes contaminated with Crag herbicide should be removed promptly and not reworn until the Crag herbicide is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where Crag herbicide or liquids containing Crag herbicide may contact the eyes.

SANITATION

- Skin that becomes contaminated with Crag herbicide should be promptly washed or showered to remove any Crag herbicide.
- Employees who handle Crag herbicide or liquids containing Crag herbicide should wash their hands thoroughly before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where solid Crag herbicide is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Crag herbicide may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of weedicides in agricultural operations	Process enclosure; local exhaust ventilation; personal protective equipment
Application of weedicides in agricultural operations	Personal protective equipment
Manufacture of Crag herbicide	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If Crag herbicide or liquids containing Crag herbicide get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If Crag herbicide or liquids containing Crag herbicide get on the skin, promptly wash the contaminated skin with water. If Crag herbicide or liquids containing Crag herbicide penetrate through the clothing, remove the clothing promptly and wash the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of Crag herbicide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When Crag herbicide or liquids containing Crag herbicide have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Crag herbicide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing Crag herbicide should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Crag herbicide may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR CRAG HERBICIDE

Condition	Minimum Respiratory Protection* Required Above 15 mg/m^3
Particulate Concentration	
75 mg/m^3 or less	Any dust and mist respirator, except single-use.
150 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRESOL, ALL ISOMERS

INTRODUCTION

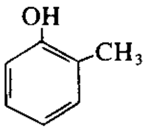
This guideline summarizes pertinent information about the three isomers of cresol (ortho-, meta-, and para-cresol) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. Throughout this guideline, the term "cresol" refers to any of the three isomers.

SUBSTANCE IDENTIFICATION

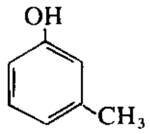
Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Formula:** C_7H_8O
- **Structure:**

(1)



(2)



(3)

- **Synonyms:** (1) o-Cresol; 2-cresol; o-cresylic acid; 1-hydroxy-2-methylbenzene; o-hydroxy toluene;
(2) m-Cresol; 3-cresol; m-cresylic acid; 1-hydroxy-3-methylbenzene; m-hydroxy toluene; 3-hydroxy toluene;
(3) p-Cresol; 4-cresol; p-cresylic acid; 1-hydroxy-4-methylbenzene; p-hydroxy toluene; 4-hydroxy toluene

- **Identifiers:** (1) CAS 95-48-7; RTECS G06300000; DOT 2076; (2) CAS 108-39-4; RTECS G06125000; DOT 2076;
(3) CAS 106-44-5; RTECS G06475000; DOT 2076;
DOT label required for all isomers: "Poison"

- **Appearance and odor:** Colorless crystals or liquid with an odor like phenol or creosote

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Physical data**

1. Molecular weight: 108.13
2. Boiling point (at 760 mmHg): (1) 191 °C (376 °F); (2) 202.7 °C (397 °F); (3) 201.9 °C (395 °F)
3. Specific gravity (water = 1): (1) 1.048; (2) 1.034; (3) 1.035
4. Vapor density (air = 1 at boiling point of cresol): 3.72
5. Melting point: (1) 30.9 °C (87.8 °F); (2) 12.0 °C (49 °F); (3) 34.8 °C (95 °F)
6. Vapor pressure at 25 °C (77 °F): (1) 0.25 mmHg; (2) 0.15 mmHg; (3) 0.11 mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): (1) 2.5; (2) 2.2; (3) 1.9
8. Evaporation rate (butyl acetate = 1): (1) 0.025; (2) 0.015; (3) 0.011
9. Saturation concentration in air (approximate) at 25 °C (77 °F): (1) 0.03% (300 ppm); (2) 0.02% (200 ppm); (3) 0.014% (140 ppm)
10. Ionization potential: (1) 8.93 eV; (2) 8.98 eV; (3) 8.97 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents, alkalies, and heat.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and formaldehyde) may be released in a fire involving cresol.
3. Caution: Liquid cresol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: (1) 81.1°C (178 °F) (closed cup); (2) 86.1°C (187 °F) (closed cup); (3) 86.1°C (187 °F) (closed cup)
2. Autoignition temperature: (1) 559 °C (1040 °F); (2) 626 °C (1158 °F); (3) 559 °C (1040 °F)
3. Flammable limits in air, % by volume: (1) Lower, 1.4 at 149 °C (300 °F); upper, not available; (2) lower, 1.1 at 150 °C (302 °F); upper, not available; (3) lower, 1.1 at 150 °C (302 °F); upper, not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

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- **Warning properties**

1. Odor threshold: Less than 1 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, cresol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, cresol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cresol is 5 parts of cresol per million parts of air (ppm) [22 milligrams of cresol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes. The NIOSH REL is 2.3 ppm (10 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cresol (all isomers)

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	5	22
NIOSH REL TWA	2.3	10
ACGIH TLV® TWA (Skin)	5	22

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cresol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats and rabbits, acute dermal absorption of cresol caused tremors, convulsions, fluid in the lungs, liver injury, and kidney inflammation; oral administration caused gastrointestinal tract inflammation, pneumonia, injury to the liver and kidneys, convulsions, and coma. Chronic inhalation of cresol by rats and mice produced inflammation and fluid accumulation in the airways, damage to the bone marrow, and degeneration of cells in the brain.
2. *Effects on humans:* Acute exposure to cresol has caused alterations in brain function and death due to respiratory failure. Repeated exposure by any route has produced nervous disorders, fluid in the lungs, and death due to severe damage to the liver, kidneys, pancreas, or spleen.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cresol can cause muscular weakness, nausea, vomiting, abdominal pain, headache, dizziness, dimness of vision, ringing in the ears, weak pulse, rapid and labored breathing, fainting, and mental confusion and depression. Skin irritation and burns can also occur. Eye contact with cresol can cause extensive damage and blindness.
2. *Long-term (chronic):* Exposure to cresol can cause difficulty in swallowing, vomiting, salivation, loss of appetite, and diarrhea. Skin eruptions, rash, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cresol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cresol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include historical and physical or laboratory findings consistent with chronic diseases of the skin or liver. In addition to the medical interview and physical examination, the means to identify these conditions may include serologic screening tests of liver function and markers for hepatitis A or B infection.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to cresol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity or physiologic function of the eyes, skin, liver, kidneys, and respiratory and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. Liver function tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, the selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cresol may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute and delayed-onset SHE's include toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to cresol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting cresol with silica gel tubes followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cresol may also be used if available. A detailed sampling and analytical method for cresol may be found in the *NIOSH Manual of Analytical Methods* (method number 2001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with cresol.

Workers should be provided with and required to use dust- and splash-proof safety goggles where cresol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cresol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cresol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cresol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cresol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cresol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cresol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cresol

Operations	Controls
During use in the manufacture of antiseptics and disinfectants, phosphate esters, antioxidants, resins, herbicides, perfumes, explosives, and photographic developers	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent and as an engine and metal cleaner; during use in the textile industry	Process enclosure, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cresol, an eyewash fountain should be provided within the immediate work area for emergency use.

If cresol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to cresol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cresol gets on the skin, wash it immediately with soap and water. If cresol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cresol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cresol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cresol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cresol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cresol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing cresol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cresol (all isomers)

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 23 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) in combination with a dust and mist filter Any supplied-air respirator Any self-contained breathing apparatus
Less than or equal to 57.5 ppm	Any supplied-air respirator operated in a continuous flow mode Any powered air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter
Less than or equal to 115 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency particulate filter Any supplied-air respirator with a full facepiece Any self-contained breathing apparatus with a full facepiece Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance reported to cause eye irritation or damage—may require eye protection) Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye damage—may require eye protection)
Less than or equal to 250 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 2.3 ppm (10 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRESOL, ALL ISOMERS

INTRODUCTION

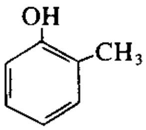
This guideline summarizes pertinent information about the three isomers of cresol (ortho-, meta-, and para-cresol) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. Throughout this guideline, the term "cresol" refers to any of the three isomers.

SUBSTANCE IDENTIFICATION

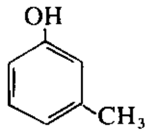
Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Formula:** C_7H_8O
- **Structure:**

(1)



(2)



(3)

- **Synonyms:** (1) o-Cresol; 2-cresol; o-cresylic acid; 1-hydroxy-2-methylbenzene; o-hydroxy toluene;
(2) m-Cresol; 3-cresol; m-cresylic acid; 1-hydroxy-3-methylbenzene; m-hydroxy toluene; 3-hydroxy toluene;
(3) p-Cresol; 4-cresol; p-cresylic acid; 1-hydroxy-4-methylbenzene; p-hydroxy toluene; 4-hydroxy toluene

- **Identifiers:** (1) CAS 95-48-7; RTECS G06300000; DOT 2076; (2) CAS 108-39-4; RTECS G06125000; DOT 2076; (3) CAS 106-44-5; RTECS G06475000; DOT 2076;
DOT label required for all isomers: "Poison"

- **Appearance and odor:** Colorless crystals or liquid with an odor like phenol or creosote

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Physical data**

1. Molecular weight: 108.13
2. Boiling point (at 760 mmHg): (1) 191 °C (376 °F); (2) 202.7 °C (397 °F); (3) 201.9 °C (395 °F)
3. Specific gravity (water = 1): (1) 1.048; (2) 1.034; (3) 1.035
4. Vapor density (air = 1 at boiling point of cresol): 3.72
5. Melting point: (1) 30.9 °C (87.8 °F); (2) 12.0 °C (49 °F); (3) 34.8 °C (95 °F)
6. Vapor pressure at 25 °C (77 °F): (1) 0.25 mmHg; (2) 0.15 mmHg; (3) 0.11 mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): (1) 2.5; (2) 2.2; (3) 1.9
8. Evaporation rate (butyl acetate = 1): (1) 0.025; (2) 0.015; (3) 0.011
9. Saturation concentration in air (approximate) at 25 °C (77 °F): (1) 0.03% (300 ppm); (2) 0.02% (200 ppm); (3) 0.014% (140 ppm)
10. Ionization potential: (1) 8.93 eV; (2) 8.98 eV; (3) 8.97 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents, alkalies, and heat.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and formaldehyde) may be released in a fire involving cresol.
3. Caution: Liquid cresol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: (1) 81.1°C (178 °F) (closed cup); (2) 86.1°C (187 °F) (closed cup); (3) 86.1°C (187 °F) (closed cup)
2. Autoignition temperature: (1) 559 °C (1040 °F); (2) 626 °C (1158 °F); (3) 559 °C (1040 °F)
3. Flammable limits in air, % by volume: (1) Lower, 1.4 at 149 °C (300 °F); upper, not available; (2) lower, 1.1 at 150 °C (302 °F); upper, not available; (3) lower, 1.1 at 150 °C (302 °F); upper, not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Warning properties**

1. Odor threshold: Less than 1 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, cresol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, cresol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cresol is 5 parts of cresol per million parts of air (ppm) [22 milligrams of cresol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes. The NIOSH REL is 2.3 ppm (10 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cresol (all isomers)

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	5	22
NIOSH REL TWA	2.3	10
ACGIH TLV® TWA (Skin)	5	22

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cresol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats and rabbits, acute dermal absorption of cresol caused tremors, convulsions, fluid in the lungs, liver injury, and kidney inflammation; oral administration caused gastrointestinal tract inflammation, pneumonia, injury to the liver and kidneys, convulsions, and coma. Chronic inhalation of cresol by rats and mice produced inflammation and fluid accumulation in the airways, damage to the bone marrow, and degeneration of cells in the brain.
2. *Effects on humans:* Acute exposure to cresol has caused alterations in brain function and death due to respiratory failure. Repeated exposure by any route has produced nervous disorders, fluid in the lungs, and death due to severe damage to the liver, kidneys, pancreas, or spleen.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cresol can cause muscular weakness, nausea, vomiting, abdominal pain, headache, dizziness, dimness of vision, ringing in the ears, weak pulse, rapid and labored breathing, fainting, and mental confusion and depression. Skin irritation and burns can also occur. Eye contact with cresol can cause extensive damage and blindness.
2. *Long-term (chronic):* Exposure to cresol can cause difficulty in swallowing, vomiting, salivation, loss of appetite, and diarrhea. Skin eruptions, rash, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cresol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

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The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

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The medical, environmental, and occupational history interviews, the physical examination, the selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cresol may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

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Acute and delayed-onset SHE's include toxic hepatitis.

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Measurements to determine worker exposure to cresol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting cresol with silica gel tubes followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cresol may also be used if available. A detailed sampling and analytical method for cresol may be found in the *NIOSH Manual of Analytical Methods* (method number 2001).

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Workers should be provided with and required to use dust- and splash-proof safety goggles where cresol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cresol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cresol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cresol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cresol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cresol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

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During use in the manufacture of antiseptics and disinfectants, phosphate esters, antioxidants, resins, herbicides, perfumes, explosives, and photographic developers	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent and as an engine and metal cleaner; during use in the textile industry	Process enclosure, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cresol, an eyewash fountain should be provided within the immediate work area for emergency use.

If cresol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to cresol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cresol gets on the skin, wash it immediately with soap and water. If cresol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cresol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cresol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cresol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cresol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cresol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing cresol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cresol (all isomers)

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 23 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) in combination with a dust and mist filter Any supplied-air respirator Any self-contained breathing apparatus
Less than or equal to 57.5 ppm	Any supplied-air respirator operated in a continuous flow mode Any powered air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter
Less than or equal to 115 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency particulate filter Any supplied-air respirator with a full facepiece Any self-contained breathing apparatus with a full facepiece Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance reported to cause eye irritation or damage—may require eye protection) Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye damage—may require eye protection)
Less than or equal to 250 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 2.3 ppm (10 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRESOL, ALL ISOMERS

INTRODUCTION

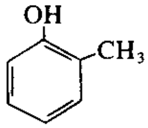
This guideline summarizes pertinent information about the three isomers of cresol (ortho-, meta-, and para-cresol) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. Throughout this guideline, the term "cresol" refers to any of the three isomers.

SUBSTANCE IDENTIFICATION

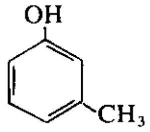
Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Formula:** C_7H_8O
- **Structure:**

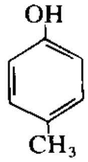
(1)



(2)



(3)



- **Synonyms:** (1) o-Cresol; 2-cresol; o-cresylic acid; 1-hydroxy-2-methylbenzene; o-hydroxy toluene;
(2) m-Cresol; 3-cresol; m-cresylic acid; 1-hydroxy-3-methylbenzene; m-hydroxy toluene; 3-hydroxy toluene;
(3) p-Cresol; 4-cresol; p-cresylic acid; 1-hydroxy-4-methylbenzene; p-hydroxy toluene; 4-hydroxy toluene

- **Identifiers:** (1) CAS 95-48-7; RTECS G06300000; DOT 2076; (2) CAS 108-39-4; RTECS G06125000; DOT 2076;
(3) CAS 106-44-5; RTECS G06475000; DOT 2076;
DOT label required for all isomers: "Poison"

- **Appearance and odor:** Colorless crystals or liquid with an odor like phenol or creosote

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Physical data**

1. Molecular weight: 108.13
2. Boiling point (at 760 mmHg): (1) 191 °C (376 °F); (2) 202.7 °C (397 °F); (3) 201.9 °C (395 °F)
3. Specific gravity (water = 1): (1) 1.048; (2) 1.034; (3) 1.035
4. Vapor density (air = 1 at boiling point of cresol): 3.72
5. Melting point: (1) 30.9 °C (87.8 °F); (2) 12.0 °C (49 °F); (3) 34.8 °C (95 °F)
6. Vapor pressure at 25 °C (77 °F): (1) 0.25 mmHg; (2) 0.15 mmHg; (3) 0.11 mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): (1) 2.5; (2) 2.2; (3) 1.9
8. Evaporation rate (butyl acetate = 1): (1) 0.025; (2) 0.015; (3) 0.011
9. Saturation concentration in air (approximate) at 25 °C (77 °F): (1) 0.03% (300 ppm); (2) 0.02% (200 ppm); (3) 0.014% (140 ppm)
10. Ionization potential: (1) 8.93 eV; (2) 8.98 eV; (3) 8.97 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents, alkalies, and heat.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and formaldehyde) may be released in a fire involving cresol.
3. Caution: Liquid cresol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: (1) 81.1°C (178 °F) (closed cup); (2) 86.1°C (187 °F) (closed cup); (3) 86.1°C (187 °F) (closed cup)
2. Autoignition temperature: (1) 559 °C (1040 °F); (2) 626 °C (1158 °F); (3) 559 °C (1040 °F)
3. Flammable limits in air, % by volume: (1) Lower, 1.4 at 149 °C (300 °F); upper, not available; (2) lower, 1.1 at 150 °C (302 °F); upper, not available; (3) lower, 1.1 at 150 °C (302 °F); upper, not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

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National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Warning properties**

1. Odor threshold: Less than 1 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, cresol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, cresol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cresol is 5 parts of cresol per million parts of air (ppm) [22 milligrams of cresol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes. The NIOSH REL is 2.3 ppm (10 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cresol (all isomers)

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	5	22
NIOSH REL TWA	2.3	10
ACGIH TLV® TWA (Skin)	5	22

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cresol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats and rabbits, acute dermal absorption of cresol caused tremors, convulsions, fluid in the lungs, liver injury, and kidney inflammation; oral administration caused gastrointestinal tract inflammation, pneumonia, injury to the liver and kidneys, convulsions, and coma. Chronic inhalation of cresol by rats and mice produced inflammation and fluid accumulation in the airways, damage to the bone marrow, and degeneration of cells in the brain.
2. *Effects on humans:* Acute exposure to cresol has caused alterations in brain function and death due to respiratory failure. Repeated exposure by any route has produced nervous disorders, fluid in the lungs, and death due to severe damage to the liver, kidneys, pancreas, or spleen.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cresol can cause muscular weakness, nausea, vomiting, abdominal pain, headache, dizziness, dimness of vision, ringing in the ears, weak pulse, rapid and labored breathing, fainting, and mental confusion and depression. Skin irritation and burns can also occur. Eye contact with cresol can cause extensive damage and blindness.
2. *Long-term (chronic):* Exposure to cresol can cause difficulty in swallowing, vomiting, salivation, loss of appetite, and diarrhea. Skin eruptions, rash, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cresol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cresol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include historical and physical or laboratory findings consistent with chronic diseases of the skin or liver. In addition to the medical interview and physical examination, the means to identify these conditions may include serologic screening tests of liver function and markers for hepatitis A or B infection.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to cresol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity or physiologic function of the eyes, skin, liver, kidneys, and respiratory and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. Liver function tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, the selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cresol may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute and delayed-onset SHE's include toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to cresol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting cresol with silica gel tubes followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cresol may also be used if available. A detailed sampling and analytical method for cresol may be found in the *NIOSH Manual of Analytical Methods* (method number 2001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with cresol.

Workers should be provided with and required to use dust- and splash-proof safety goggles where cresol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cresol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cresol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cresol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cresol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cresol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cresol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cresol

Operations	Controls
During use in the manufacture of antiseptics and disinfectants, phosphate esters, antioxidants, resins, herbicides, perfumes, explosives, and photographic developers	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent and as an engine and metal cleaner; during use in the textile industry	Process enclosure, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cresol, an eyewash fountain should be provided within the immediate work area for emergency use.

If cresol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to cresol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cresol gets on the skin, wash it immediately with soap and water. If cresol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cresol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cresol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cresol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cresol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cresol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing cresol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cresol (all isomers)

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 23 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) in combination with a dust and mist filter Any supplied-air respirator Any self-contained breathing apparatus
Less than or equal to 57.5 ppm	Any supplied-air respirator operated in a continuous flow mode Any powered air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter
Less than or equal to 115 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency particulate filter Any supplied-air respirator with a full facepiece Any self-contained breathing apparatus with a full facepiece Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance reported to cause eye irritation or damage—may require eye protection) Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye damage—may require eye protection)
Less than or equal to 250 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 2.3 ppm (10 mg/m^3) (TWA).

Occupational Health Guideline for Crotonaldehyde

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH=CHCHO$
- Synonyms: Beta-methylacrolein; propylene aldehyde; crotonic aldehyde; 2-butenal
- Appearance and odor: Colorless to straw-colored liquid with an irritating, pungent, and suffocating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for crotonaldehyde is 2 parts of crotonaldehyde per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of crotonaldehyde per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Crotonaldehyde can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Crotonaldehyde causes irritation of the eyes, nose, and throat. It may also cause an irritation of the skin and difficulty in breathing which may occur several hours after exposure.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to crotonaldehyde.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to crotonaldehyde at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from crotonaldehyde exposure.

—Chronic respiratory disease: Crotonaldehyde causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of crotonaldehyde might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Crotonaldehyde is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Crotonaldehyde vapor irritates the eyes and respiratory tract. Rats did not survive exposure to 1650 ppm for 10 minutes; there was respiratory distress, an excitatory stage, and terminal convulsions; autopsy revealed bronchiolar damage. Pulmonary edema has also been observed in rats dead of exposure to 1500 ppm for 30 minutes. Human subjects exposed to 45 ppm for a few seconds experienced conjunctival irritation; at 15 ppm there was no eye discomfort. The liquid when placed in the eyes of rabbits caused severe injury. In a series of eight cases of corneal injury from industrial exposure to crotonaldehyde, healing was complete in 48 hours; the severity of exposure was not specified. A case of apparent sensitization of undetermined nature to crotonaldehyde has been reported in a laboratory worker.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 70.1

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Occupational Safety and Health Administration

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2. Boiling point (760 mm Hg): 102 C (216 F)
3. Specific gravity (water = 1): 0.85
4. Vapor density (air = 1 at boiling point of crotonaldehyde): 2.4
5. Melting point: −75 C (−103 F)
6. Vapor pressure at 20 C (68 F): 30 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 15.5
8. Evaporation rate (butyl acetate = 1): 2.7

- **Reactivity**

1. Conditions contributing to instability: Heat may cause polymerization to occur and containers to burst.
2. Incompatibilities: Contact with caustics, ammonia, organic amines, and mineral acids may cause violent polymerization to occur. Contact with strong oxidizers may cause fires and explosions. Crotonaldehyde is readily converted by oxygen to peroxides and acids.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving crotonaldehyde.
4. Special precautions: Liquid crotonaldehyde will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 12.8 C (55 F) (closed cup)
2. Autoignition temperature: 232 C (450 F)
3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 15.5
4. Extinguishant: Carbon dioxide, dry chemical, alcohol foam

- **Warning properties**

1. Odor Threshold: Stern and May report odor thresholds for crotonaldehyde of 0.062 and 0.035 ppm, respectively.
2. Eye Irritation Level: Both Grant and the *Documentation of TLV's* report that "humans have experienced "considerable eye discomfort" at 45 ppm for a brief exposure (a few seconds). Humans did not experience eye irritation during an exposure of a few seconds to 15 ppm. The threshold of eye irritation is not given, however.
3. Other Information: According to the *Documentation of TLV's*, crotonaldehyde is also a respiratory tract irritant. The threshold limit was recommended "to prevent irritation of eyes and respiratory passages."
4. Evaluation of Warning Properties: Since the odor threshold of crotonaldehyde is below the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for crotonaldehyde is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid crotonaldehyde or liquids containing crotonaldehyde, where skin contact may occur.
- Clothing wet with liquid crotonaldehyde or liquids containing crotonaldehyde should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of crotonaldehyde from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the crotonaldehyde, the person performing the operation should be informed of crotonaldehyde's hazardous properties.
- Where exposure of an employee's body to liquid crotonaldehyde or liquids containing crotonaldehyde may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with and non-impervious clothing which becomes contaminated with crotonaldehyde should be removed immediately and not reworn until the crotonaldehyde is removed from the clothing.
- Employees should be provided with and required to

use splash-proof safety goggles where there is any possibility of liquid crotonaldehyde or liquids containing crotonaldehyde contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquid crotonaldehyde or liquids containing more than 1% of crotonaldehyde by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with crotonaldehyde should be immediately washed or showered to remove any crotonaldehyde.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to crotonaldehyde may occur and control methods which may be effective in each case:

Operation	Controls
Use an an intermdediate in manufacture of butyl alcohol; use in polymer technology as a reaction medium, formulator, adhesive, antioxidant, corrosion inhibitor, and stabilizer	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis in manufacture of dyestuffs, sedatives, pesticides, and flavoring agents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for purification of mineral and lubricating oils; use during manufacture of surface active agents as bactericides for petroleum well fluids, metal brighteners, and leather/paper sizing materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture as warning agent in fuel gases for locating breaks and leaks in pipes; use in leather tanning and preparation of tanning materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of rubber and rubber antioxidants and accelerators; use in manufacture of chemical warfare agents; use in photographic emulsion as a hardening agent for gelatin	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid crotonaldehyde or liquids containing crotonaldehyde get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid crotonaldehyde or liquids containing crotonaldehyde get on the skin, immediately flush the contaminated skin with water. If liquid crotonaldehyde or liquids containing crotonaldehyde soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of crotonaldehyde, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When crotonaldehyde has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If crotonaldehyde or liquids containing crotonaldehyde are spilled or leaked, the following steps should be take

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Liquid crotonaldehyde should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of crotonaldehyde vapors are permitted.

- Waste disposal method:

Crotonaldehyde may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR CROTONALDEHYDE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Vapor Concentration	
100 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
400 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 400 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRUFOMATE

INTRODUCTION

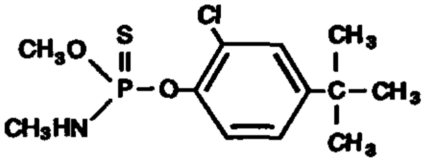
This guideline summarizes pertinent information about crufomate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{19}ClNO_3P$

- **Structure**



- **Synonyms**

Amidofos; 4-tert-butyl-2-chlorophenyl methyl methylphosphoramidate; Dowco 132; Montrel; o-methyl-o-2-chloro-4-tert-butylphenyl N-methylamidophosphate; Ruelene

- **Identifiers**

1. CAS No.: 299-86-5
2. RTECS No.: TB3850000
3. DOT UN: 2765 55 (phenoxy pesticides, solid, toxic, n.o.s.)
4. DOT label: Poison or St. Andrew's Cross (depending on quantity shipped)

- **Appearance and odor**

Crufomate is a white, crystalline solid in pure form; the commercial product is a yellow oil. Crufomate is an organophosphorus pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data

1. Molecular weight: 291.7
2. Boiling point (0.01 mm Hg): 117° to 118°C (242.6° to 244.4°F)
3. Specific gravity (water = 1): 1.2 at 70°C (158°F)
4. Vapor density: Not applicable
5. Melting point: 60° to 60.5°C (140° to 141°F) (pure); 58.7°C (137.7°F) (92%, technical grade)

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6. Vapor pressure at 117°C (242.6°F): 0.01 mm Hg

7. Solubility: Practically insoluble in water and light petroleum; soluble in benzene, alcohol, ethyl ether, cyclohexane, carbon tetrachloride, and acetonitrile.

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, open flame, strong alkalies, and strong acids. Crufomate is unstable over long periods of time, in water preparations, and at temperatures above 60°C (140°F).

2. Incompatibilities: Crufomate decomposes in strongly alkaline (greater than pH 7) and strongly acidic media.

3. Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen, and chlorine) may be released in a fire involving crufomate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to crufomate.

1. Flash point: 41.1° to 60°C (106° to 140°F), depending on the formulation

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam for small fires. Water spray, fog, or standard foam is recommended to fight large fires involving crufomate.

Fires involving crufomate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of crufomate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving crufomate. Chemical protective clothing that is specifically recommended for crufomate may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving crufomate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for crufomate [29 CFR 1910.1000, Table Z- 1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a 15-min short-term exposure limit (STEL). A STEL is a 15-min TWA concentration that should not be exceeded at any time during a workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned crufomate a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of neurotoxicity and cholinesterase inhibition. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to crufomate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to crufomate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, crufomate is an inhibitor of plasma and erythrocyte cholinesterase.

Application of crufomate to the eye of rabbits as undiluted or 10% solutions resulted in corneal cloudiness and conjunctival irritation, along with slight pain [Clayton and Clayton 1982; ACGIH 1991]. Crufomate produced slight erythema when applied undiluted or as a 10% solution to the abraded or intact skin of the rabbit [Clayton and Clayton 1982; ACGIH 1991]. The dermal LD_{50} in rabbits is 2,000 mg/kg [NIOSH 1992b]. The lowest toxic inhalation dose in rats is 12 mg/m^3 for 4 hr [NIOSH 1992b]. The oral LD_{50} is 460 mg/kg in rats, 400 mg/kg in rabbits, and 1,000 mg/kg in guinea pigs [NIOSH 1992b]. Dogs fed 250 ppm crufomate in the diet for 75 days exhibited depression of blood cholinesterase and slight liver morphological changes; no effects were observed in dogs given dietary doses of 40 or 125 ppm [Clayton and Clayton 1982]. In 90-day dietary studies in rats, blood and/or brain cholinesterase levels were depressed 40% to 60% as compared with levels in untreated controls when doses of 30 to 1,000 ppm (1.5 to 50 mg/kg/day) were administered; no other adverse effects were observed in these animals [Clayton and Clayton 1982]. Rats fed 1,000 ppm (50 mg/kg/day) for 2 years showed marked cholinesterase inhibition, growth retardation, atrophy of the muscles of the hind limbs, and slight degeneration of the sciatic nerve; after 12, 18, or 24 months on this regimen, there was a 50% reduction in testes weights, reflecting degeneration and atrophy of the seminiferous tubules [Clayton and Clayton 1982]. No teratologic or reproductive effects were seen in male and female rats fed up to 500 ppm crufomate (25 mg/kg/day) for three generations [Clayton and Clayton 1982]. In female mice treated dermally with 50 or 100 mg/kg crufomate on days 35 and 21 before mating, the lower dose prolonged the gestation period and decreased the index of lactation and the higher dose reduced conception rate, litter size, and lactation index and decreased fetal body weight [NLM 1992].

2. *Effects on Humans:* In humans, crufomate is a moderately potent cholinesterase inhibitor.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute overexposure to crufomate by the oral route may cause severe gastrointestinal effects such as cramps, diarrhea, nausea, and anorexia. Acute inhalation exposure can cause wheezing, difficult breathing, blurred vision, and tearing. Dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Continued low-level exposure to crufomate may lead to acetylcholine buildup, causing the signs and symptoms of systemic poisoning described above for acute overexposure.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air immediately. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if crufomate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve crufomate and may result in worker exposures to this substance:

—Manufacture of crufomate and crufomate-containing pesticides

—Formulation and application of crufomate and crufomate-containing pesticides

—Use as a selective insecticide against cattle grubs, horn flies, and lice

The following methods are effective in controlling worker exposures to crufomate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to crufomate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A pre-exposure plasma and red blood cell cholinesterase activity baseline should also be established.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to crufomate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma and red blood cell cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to crufomate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of crufomate on the levels of plasma or red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Absorption of crufomate can be confirmed by analysis of urine for its metabolite, crufomate phenol. However, correlations between airborne and urinary levels of crufomate and its metabolite have not been established. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as crufomate. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for crufomate (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne crufomate is determined by using an OSHA Versatile Sampler (OVS-2) with a 13 mm XAD-2 tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in OSHA's Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If crufomate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with crufomate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of crufomate.

A worker who handles crufomate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where crufomate or a solution containing crufomate is handled, processed, or stored.

STORAGE

Crufomate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Crufomate is unstable over long periods of time in water preparations and at temperatures above 60°C (140°F). Containers of crufomate must be stacked in a manner that permits free circulation of air below and inside the pile of containers. Containers of crufomate should be protected from physical damage and should be stored separately from strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained crufomate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving crufomate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Water spray may be used to reduce vapors.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the crufomate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Crufomate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of crufomate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of crufomate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although crufomate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of crufomate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with crufomate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to crufomate permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated some resistance to permeation by these compounds: a laminate of Viton and neoprene, or a laminate of butyl rubber and neoprene. Since specific test data are not available for crufomate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to crufomate.

If crufomate is dissolved an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which crufomate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with crufomate.

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Occupational Health Guideline for Cumene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5C_3H_7$
- Synonyms: Isopropylbenzene; 2-phenylpropane; cumol
- Appearance and odor: Colorless liquid with a sharp, penetrating, and aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cumene is 50 parts of cumene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 245 milligrams of cumene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cumene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Cumene may cause irritation of the skin and eyes. It may also cause dizziness, drowsiness, slight incoordination, and unconsciousness.

2. Long-term Exposure: Prolonged or repeated exposure to cumene may cause skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cumene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cumene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cumene exposure.

—Kidney disease: Although cumene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cumene might cause exacerbation of symptoms due to its irritant properties or pyschic reflex bronchospasm.

—Liver disease: Although cumene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: Cumene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The main toxic effect of cumene is irritation of the eyes, skin, and upper respiratory tract. Narcosis has been reported to occur in animals on high exposure. There are no reports of systemic effects in man as a result of industrial exposure. Chronic exposure of rats above 500 ppm causes congestion of lungs, liver, and kidneys, but no bone marrow changes.

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Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 120
2. Boiling point (760 mm Hg): 152 C (306 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of cumene): 4.14
5. Melting point: −96 C (−141 F)
6. Vapor pressure at 20 C (68 F): 8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Very low

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cumene.
4. Special precautions: None

- **Flammability**

1. Flash point: 44 C (111 F) (closed cup)
2. Autoignition temperature: 425 C (797 F)
3. Flammable limits in air, % by volume: Lower: 0.9; Upper: 6.5
4. Extinguishant: Water spray, dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* and the ILO both report that the odor of cumene is detectable at very low levels. May reports an odor threshold for cumene of 1.2 ppm.
2. Eye Irritation Level: The *Documentation of TLV's* notes that cumene is an eye irritant, but the concentrations producing irritation are not given.
3. Evaluation of Warning Properties: Since the odor threshold of cumene is below the permissible exposure limit, cumene is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cumene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cumene may be used. An analytical method for cumene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed:, Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cumene.
- Clothing wet with liquid cumene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cumene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cumene, the person performing the operation should be informed of cumene's hazardous properties.
- Non-impervious clothing which becomes wet with liquid cumene should be removed promptly and not reworn until the cumene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid cumene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid cumene should be promptly washed or showered with soap or mild detergent and water to remove any cumene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cumene may occur and control methods which may be effective in each case:

Operation	Controls
Use during organic synthesis, particularly the cumene route to phenol and 2-methyl styrene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a constituent of solvents in 150 to 160 C boiling point; use during application of lacquers, paints, and enamels as thinner	General dilution ventilation; personal protective equipment
Use in petroleum distillates either alone or in solvent formulation and surface coating processes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during mixing and blending of fuels, especially aviation	General dilution ventilation; personal protective equipment
Liberation during petroleum refining processes; during production of styrene by cracking	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cumene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If cumene gets on the skin, promptly flush the contaminated skin with water. If cumene soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of cumene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If cumene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If cumene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid. Cumene liquid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Cumene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid.

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RESPIRATORY PROTECTION FOR CUMENE

Condition	**Minimum Respiratory Protection* Required Above 50 ppm**
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs at this level, a full facepiece respirator should be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN

INTRODUCTION

This guideline summarizes pertinent information about cyanogen for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $(CN)_2$

- **Synonyms**

  Carbon nitride, dicyan, dicyanogen, ethane dinitrile, nitriloacetonitrile, oxalic acid dinitrile, oxalic nitrile, oxalonitrile, oxalyl cyanide, prussite

- Identifiers

  1. CAS No.: 460-19-5
  2. RTECS No.: GT1925000
  3. DOT UN: 1026 18
  4. DOT label: Poison Gas; Flammable Gas

- **Appearance and odor**

  Cyanogen is a highly flammable, colorless gas with a pungent, penetrating, almond-like odor; this substance is shipped as a liquefied gas under its own vapor pressure. The odor threshold is reported to be 250 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 52.04
  2. Boiling point (760 mm Hg): -21.17°C (-6.1°F)
  3. Specific gravity (for the liquid) (water = 1): 0.95 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyanogen): 1.8
  5. Melting point: -27.9°C (-18.2°F)
  6. Vapor pressure at 21°C (69.9°F): 3,868.4 mm Hg
  7. Solubility: Soluble in water, alcohol, and ether
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, shock, and direct sunlight

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2. Incompatibilities: Contact of cyanogen with acids or their vapors, water, liquid oxygen, or oxidizers (such as chlorine, fluorine, or bromine) causes explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as cyanide, hydrogen cyanide, carbon monoxide, and oxides of nitrogen) may be released in a fire involving cyanogen.

4. Special precautions: Cyanogen is denser than air and can collect in enclosed spaces. It can flow along the surface, reach distant, low-lying sources of ignition, and flash back.

Flammability

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to cyanogen.

1. Flash point: Cyanogen has a wide range of explosiveness.

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 6.6; upper, 32

4. Extinguishant: Let the fire burn unless the leak can be stopped immediately. Use water spray, fog, or standard foam to fight large fires involving cyanogen. Water may be used to cool fire-exposed containers and to protect persons attempting to stop the leak.

Fires involving cyanogen should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Cyanogen is heavier than air and may travel to a source of ignition and flash back. Containers of cyanogen may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen. Chemical protective clothing that is specifically recommended for cyanogen may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (20 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen a threshold limit value (TLV) of 10 ppm (21 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and respiratory irritation associated with cyanogen exposure. The ACGIH limit is based on the risk of irritant and systemic effects associated with exposure to cyanogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyanogen can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Cyanogen is a highly toxic gas that causes severe irritation, respiratory distress, and death on acute exposure. Rabbits survived dermal exposure to 10,000 ppm for 8 hours without apparent systemic effects [McNerney and Schrenk 1960]. The

LC_{50} in rats is 350 ppm for 1 hr [NIOSH 1990]. Acutely poisoned animals showed signs of respiratory distress and severe eye irritation before death [NIOSH 1990]. Monkeys and rats exposed for 6 hr/day, 5 days/week to 11 or 25 ppm of cyanogen for 6 months showed no hematologic, clinical, or histopathological changes attributable to exposure [NLM 1992].

2. *Effects on Humans:* Cyanogen causes cellular hypoxia in humans; in lethal amounts, it causes respiratory and central nervous system stimulation, followed by headache, vertigo, agitation followed by combative behavior, coma, convulsions, respiratory arrest, and death [NLM 1992]. Cyanogen reacts readily with cytochrome oxidase in mitochondria which inhibits tissue oxidation resulting in cytotoxic hypoxia. In addition to hypoxia, exposure to cyanogen causes eye, nose, and upper respiratory tract irritation. Exposure to a concentration of 16 ppm for 6 to 8 min caused irritation, but exposure to 8 ppm for the same interval caused no irritation [McNerney and Schrenk 1960].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen may cause pain, redness, and tearing of the eyes, runny nose, and difficult breathing; if the overexposure is severe, the following signs of cyanide poisoning are seen: cherry red lips, tachypnea and hyperpnea (followed by bradycardia), headache, vertigo, agitation, behavioral changes, and convulsions.

2. *Chronic exposure:* The signs and symptoms of chronic overexposure to cyanogen include those of thyroid dysfunction: dizziness, loss of appetite, and weight loss.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL

The following operations may involve cyanogen and may result in worker exposures to this substance:

—Use as an intermediate in organic synthesis

—Use as a fumigant

—Use for welding and cutting heat-resistant metals

—Use as a rocket and missile propellant

The following methods are effective in controlling worker exposures to cyanogen, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyanogen, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and thyroid.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyanogen at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or thyroid.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyanogen exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyanogen on the respiratory system or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen is determined by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh) coated with 10% (w/w) 2-(hydroxymethyl) piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 12 liters is collected. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cyanogen contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cyanogen should be removed immediately.

A worker who handles cyanogen should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyanogen is handled, processed, or stored.

STORAGE

Cyanogen should be stored in pressurized, secured, airtight containers in a cool, dry, well-ventilated area; the containers must be labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must meet requirements for a Class I flammable liquid. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Ventilation systems used in cyanogen storage areas must be maximally explosion proof. Containers of cyanogen should be protected from physical damage and should be stored separately from water, acids, acid vapors, and oxidizers. Containers should also be protected from shock, direct sunlight, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters. Only non sparking tools may be used to handle cyanogen. To prevent static sparks, containers should be grounded and bonded for transfers.

LEAKS

In the event of a leak involving cyanogen, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyanogen is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for cyanogen is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of cyanogen per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA [49 CFR 372.30] reporting the amount of cyanogen emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P031. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyanogen exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing, as appropriate) should be worn to prevent any skin contact with liquid cyanogen. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen.

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen. Contact lenses should not be worn if the potential exists for cyanogen exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about cyanogen chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $ClCN$

- **Structure**

  $N\equiv CCl$

- **Synonyms**

  Chlorcyan; chlorine cyanide; chlorocyanide; chlorocyanogen

- **Identifiers**

1. CAS No.: 506-77-4
2. RTECS No.: GT2275000
3. DOT UN: 1589 15 (for cyanogen chloride containing less than 0.9% water)
4. DOT label: Poison gas; Flammable gas

- **Appearance and odor**

  Cyanogen chloride is a colorless gas with a pungent, penetrating odor. It is shipped in steel cylinders under its own vapor pressure as a liquefied gas. The odor threshold of cyanogen chloride is 1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 61.5
2. Boiling point (760 mm Hg): 13.8°C (56.8°F)
3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of cyanogen chloride): 2.16
5. Melting point: -6°C (21.2°F)
6. Vapor pressure at 20°C (68°F): 1,000 to 1,010 mm Hg
7. Solubility: Soluble in water, alcohol, ether, and all organic solvents

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Moisture, sparks, heat, or flame
2. Incompatibilities: Contact of cyanogen chloride with water, steam, acids, acid salts, or strong oxidizing agents may cause fires or explosions.
3. Hazardous decomposition products: Toxic substances (such as the oxides of nitrogen cyanide, cyanide, chloride ions, and hydrogen cyanide) may be released in a fire involving cyanogen chloride.
4. Special precautions: Crude cyanogen chloride trimerizes violently to cyanuric chloride if catalyzed by traces of hydrogen chloride or ammonium chloride.

Flammability

The National Fire Protection Association has not assigned a flammability rating to cyanogen chloride. However, the Hazardous Materials Identification System (HMIS) developed by the National Paint and Coatings Association assigns cyanogen chloride a flammability rating of 4 (severe fire hazard).

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving cyanogen chloride.

Fires involving cyanogen chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cyanogen chloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Take care not to permit water to contact the cyanogen chloride inside the containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen chloride. Chemical protective clothing that is specifically recommended for cyanogen chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen chloride.

EXPOSURE LIMITS

- **OSHA PEL**

  The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

  The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.3 ppm (0.6 mg/m^3) as a ceiling limit [NIOSH 1992].

- **ACGIH TLV**

  The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen chloride a ceiling limit value of 0.3 ppm (0.75 mg/m^3) [ACGIH 1993].

- **Rationale for limits**

  The NIOSH limit is based on the risk of severe eye and pulmonary irritation [NIOSH 1992]. The ACGIH limit is based on the risk of irritant, metabolic, and respiratory effects associated with exposure to cyanogen chloride [ACGIH 1993].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

  Exposure to cyanogen chloride can occur through inhalation, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

  1. *Effects on Animals:* Cyanogen chloride causes eye, mucous membrane, skin, and upper respiratory tract

irritation in animals. Although experimental data on skin absorption are lacking, this substance is reported to cause systemic toxicity when absorbed through the skin in toxic amounts [NLM 1992]. The LC_{50} in rats is 5,400 mg/m^3 (2,700 ppm) for 3 min; in monkeys, it is 4,400 mg/m^3 (2,200 ppm) for 1 min; and in rabbits, it is 6,000 mg/m3 (3,000 ppm) for 7 min [NIOSH 1993]. Animals acutely poisoned with cyanogen chloride show signs of cyanide poisoning and pulmonary edema (dyspnea, bloody nasal exudate, cyanosis) before death [ACGIH 1991].

2. *Effects on Humans:* Cyanogen chloride is a severe eye, skin, mucous membrane, and upper respiratory tract irritant in humans. Exposure to cyanogen chloride also causes cellular hypoxia, as is the case with other cyanides. Exposure to concentrations of cyanogen chloride below 1 ppm (approximately 0.7 ppm) causes burning of the eyes, lacrimation, and severe blepharospasm, local skin irritation, and marked respiratory tract irritation, with hemorrhagic changes and pulmonary edema [Grant 1986; NLM 1992; ACGIH 1991]. Cyanide also interferes with the cell's ability to utilize oxygen, which leads to cellular hypoxia, headache, dizziness, and signs and symptoms that include seizures and coma. Exposure to a cyanogen chloride concentration of 48 ppm for 30 min or to a 159-ppm concentration for 10 min has caused death in humans [Clayton and Clayton 1982]. Repeated inhalation of low (not further specified) concentrations of cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, and weight loss [NLM 1992]. Workers chronically exposed to cyanide salts during metal heat-treating operations developed enlarged thyroid glands [ACGIH 1991; NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen chloride may cause burning of the eyes, tearing, and spasms of the eyelids; a bitter, burning taste followed by a feeling of constriction in the mouth; sweating, salivation, nausea, and vomiting; anxiety confusion, vertigo, giddiness, dizziness, and headache; a bright pink or brick-red coloration to the skin; difficult breathing; increased or decreased blood pressure and heart rate; seizures; and an increase in respiratory rate followed by respiratory arrest.

2. *Chronic exposure:* Chronic overexposure to cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, weight loss, and enlargement of the thyroid.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyanogen chloride and may result in worker exposures to this substance:

—Use in organic synthesis

—Military use as a poison and tear gas

—Use as a warning agent in fumigant gases

—Use in ore refining, in the production of synthetic rubber, and as a metal cleaner

—Use in the Lonza process to produce extremely pure malononitrile

The following methods are effective in controlling worker exposures to cyanogen chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyanogen chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and thyroid. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyanogen chloride at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or thyroid.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyanogen chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyanogen chloride on the respiratory system or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen chloride have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen chloride is determined by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh). The coating is 10% (w/w) 2-(hydroxymethyl)piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min. The sample is then treated with toluene to extract the cyanogen chloride. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is described in the OSHA Computerized Information System [OSHA 1992].

PERSONAL HYGIENE

Cyanogen chloride can be absorbed through the skin in toxic amounts. Therefore, if cyanogen chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyanogen chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyanogen chloride, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles cyanogen chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyanogen chloride or a solution containing cyanogen chloride is handled, processed, or stored.

STORAGE

Cyanogen chloride gas or liquid should be stored in a cool, dry, well-ventilated area in pressurized, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cyanogen chloride should not be exposed to direct sunlight. Containers of cyanogen chloride should be protected from shock or physical damage and should be stored separately from water, acids, acid vapors, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained cyanogen chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyanogen chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Evacuate all nonessential personnel.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.
6. Do not get water inside container.
7. For small liquid spills, flush area with flooding amounts of water.
8. For large liquid spills, build dikes far ahead of the spill to contain the cyanogen chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyanogen chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for cyanogen chloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyanogen chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen chloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P033. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen chloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyanogen chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing) should be worn as necessary to prevent any skin contact with cyanogen chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen chloride permeation; however, butyl rubber is reported to provide no more than 1 hr of resistance against permeation by cyanogen bromide, a chemically similar substance. Since specific test data are not available for cyanogen chloride, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen chloride.

If cyanogen chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen chloride gas or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen chloride. Contact lenses should not be worn if the potential exists for cyanogen chloride exposure.

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Occupational Health Guideline for Cyclohexane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_{12}
- Synonyms: Hexahydrobenzene; hexamethylene; benzene hexahydride
- Appearance and odor: Colorless liquid with mild, sweet odor resembling chloroform or benzene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclohexane is 300 parts of cyclohexane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1050 milligrams of cyclohexane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexane can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to cyclohexane may cause dizziness and nausea. At higher levels of exposure, a person may become unconscious. Liquid splashes of cyclohexane may iritate the eyes.

2. Long-term Exposure: Prolonged or repeated exposures can cause skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclohexane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclohexane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclohexane exposure.

—Skin disease: Cyclohexane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although cyclohexane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexane might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although cyclohexane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Cyclohexane is primarily a local irritant and central nervous system depressant. The depressant effect is from exposure to conconcentrations above 12,000 ppm, while prolonged or repeated exposure to concentrations above 300 ppm produces a mild irritation of the eyes and upper respiratory tract. Aspiration causes a chemical pneumonitis.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 84
2. Boiling point (760 mm Hg): 80 C (177 F)
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of cyclohexane): 2.98
5. Melting point: 6.5 C (44 F)
6. Vapor pressure at 20 C (68 F): 95 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.01
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexane.
4. Special precautions: None

- **Flammability**

1. Flash point: −20 C (−4 F) (closed cup)
2. Autoignition temperature: 245 C (473 F)
3. Flammable limits in air, % by volume: Lower: 1.31; Upper: 8.35
4. Extinguishant: Dry chemical, foam, or carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports that the odor threshold of cyclohexane is 0.41 ppm. The Manufacturing Chemists Association (MCA) reports that "the sweetish odor of cyclohexane, which resembles that of chloroform, is not adequate warning against exposure to hazardous concentrations." The AIHA *Hygienic Guide* reports similar information.
2. Eye Irritation Level: The *Documentation of TLV's* reports that, according to Gerarde, a concentration of 300 ppm is somewhat irritating to the eyes. The MCA, however, states that even in high concentrations the vapor is not irritating to the eyes.
3. Evaluation of Warning Properties: Since the MCA and the *Hygienic Guide* both state that the odor of cyclohexane is not sufficient warning against exposure to hazardous concentrations, and since MCA states that even high concentrations of cyclohexane do not cause eye irritation, for the purposes of this guideline, cyclohexane is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cyclohexane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cyclohexane may be used.

An analytical method for cyclohexane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cyclohexane.
- Clothing wet with liquid cyclohexane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclohexane, the person performing the operation should be informed of cyclohexane's hazardous properties.
- Any clothing which becomes wet with liquid cyclohexane should be removed immediately and not reworn until the cyclohexane is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid cyclohexane may contact the eyes.

SANITATION

- Skin that becomes wet with cyclohexane should be promptly washed or showered with soap or mild detergent and water to remove any cyclohexane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclohexane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent to dissolve cellulose ethers, resins, fats, waxes, oils, bitumin, and crude rubber; use in perfume manufacture; use during surface coating operations (lacquers)	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of adipic acid for production of Nylon 66 and engineering plastics	Process enclosure; local exhaust ventilation; personal protective equipment
Use during synthesis of caprolactam in Nylon 6 production	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cyclohexane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If cyclohexane gets on the skin, promptly flush the contaminated skin with water. If cyclohexane soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of cyclohexane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If cyclohexane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If cyclohexane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid. Cyclohexane liquid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Cyclohexane may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

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RESPIRATORY PROTECTION FOR CYCLOHEXANE

Condition	**Minimum Respiratory Protection* Required Above 300 ppm**
Vapor Concentration	
3000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
10,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Cyclohexanol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_{11}OH$
- Synonyms: Hexalin; hydroxycyclohexane; hydralin; anol; hexahydrophenol; cyclohexyl alcohol
- Appearance and odor: Colorless, viscous liquid or sticky solid with a faint, camphor-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclohexanol is 50 parts of cyclohexanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 200 milligrams of cyclohexanol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexanol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to cyclohexanol may cause headache and irritation of the eyes, nose, and throat.

2. *Long-term Exposure:* Repeated exposure to cyclohexanol may cause irritation of the skin.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclohexanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclohexanol at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclohexanol exposure.

—Skin disease: Cyclohexanol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although cyclohexanol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although cyclohexanol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexanol might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Cyclohexanol vapor has a narcotic effect at high concentrations and causes irritation of the eyes, nose, and throat. Prolonged exposure at 145 ppm resulted in minimal changes in the liver and kidneys of rabbits. Lethargy occurs in the monkey at 700 ppm, and narcosis in rabbits at 1000 ppm. The liquid defats the skin and may produce dermatitis upon prolonged or frequent contact. No chronic systemic effects have been reported in humans.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): 161 C (322 F)
3. Specific gravity (water = 1): 0.96
4. Vapor density (air = 1 at boiling point of cyclohexanol): 3.5
5. Melting point: 23.6 C (75 F)
6. Vapor pressure at 20 C (68 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 3.6
8. Evaporation rate (butyl acetate = 1): 0.08

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexanol.
4. Special precautions: Cyclohexanol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 67.8 C (154 F (closed cup)
2. Autoignition temperature: 300 C (572 F)
3. Flammable limits in air, % by volume: Lower: 2.4 (calculated at flash point)
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Irritation Levels: The *Documentation of TLV's* states that "Nelson and his associates found 100 ppm of cyclohexanol to be objectionable to the ten persons subjected to this concentration in a study of sensory response to a number of solvent vapors. In this study the individuals classified the effect of the vapor on the eyes, nose, and throat after 3 to 5 minutes' exposure as objectionable. The limit of 50 ppm was chosen to reduce objectionable irritation."
3. Evaluation of Warning Properties: Since cyclohexanol is known to produce eye, nose, and throat irritation at a concentration only twice the permissible exposure limit, it is treated as a substance with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cyclohexanol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cyclohexanol may be used. An analytical method for cyclohexanol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid cyclohexanol.
- Clothing wet with liquid cyclohexanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclohexanol, the person performing the operation should be informed of cyclohexanol's hazardous properties.
- Non-impervious clothing which becomes contaminated with solid or liquid cyclohexanol should be removed promptly and not reworn until the cyclohexanol is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid cyclohexanol may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid or solid cyclohexanol should be promptly washed or showered with soap or mild detergent and water to remove any cyclohexanol.
- Employees who handle liquid or solid cyclohexanol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclohexanol may occur and control methods which may be effective in each case:

Operation	Controls
Use during synthesis of adipic acid, primarily in production of Nylon 66	General dilution ventilation; personal protective equipment
Liberation during synthesis of caprolactam	General dilution ventilation
Use during application of surface coatings of natural and synthetic textile dyes, cotton mercerizers, paints, varnishes, lacquers, and shellacs	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in cleaning and degreasing operations	Local exhaust ventilation; personal protective equipment
Use in production of dicyclohexyl phthalate, other cyclohexyl esters, soaps, synthetic detergents, and rubber cement	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cyclohexanol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If cyclohexanol gets on the skin, promptly wash the contaminated skin with water. If cyclohexanol soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of cyclohexanol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When cyclohexanol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If cyclohexanol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, mixed with ethyl alcohol, and atomized in a suitable combustion chamber.

- Waste disposal methods:

Cyclohexanol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By mixing with ethyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR CYCLOHEXANOL

Condition	**Minimum Respiratory Protection*** **Required Above 50 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3500 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

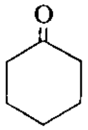
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLOHEXANONE

INTRODUCTION

This guideline summarizes pertinent information about cyclohexanone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{10}O$
- **Structure:**



- **Synonyms:** Anone, hexanon, ketohexamethylene, nadone, pimelic ketone, pimelin ketone
- **Identifiers:** CAS 108-94-1; RTECS GW1050000; DOT 1915, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless to slightly yellow liquid with an odor like peppermint

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.16
2. Boiling point (at 760 mmHg): 155.6°C (312°F)
3. Specific gravity (water = 1): 0.95
4. Vapor density (air = 1 at boiling point of cyclohexanone): 3.4
5. Melting point: -47°C (-52.6°F)
6. Vapor pressure at 20°C (68°F): 2 mmHg; at 25°C (77°F), 4.5 mmHg
7. Slightly soluble in water
8. Evaporation rate (butyl acetate = 1): 0.23
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.26% (2,600 ppm); at 25°C (77°F), 0.60% (6,000 ppm)
10. Ionization potential: 9.14 eV

- **Reactivity**

1. Incompatibilities: Cyclohexanone may react with oxidizing agents and nitric acid causing fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving cyclohexanone.
3. Caution: Cyclohexanone will dissolve most plastics, resins, and rubber.

- **Flammability**

1. Flash point: 43.9°C (111°F) (closed cup)
2. Autoignition temperature: 420°C (788°F)
3. Flammable limits in air, % by volume: Lower, 1.1; Upper, 9.4
4. Extinguishant: Alcohol foam, dry chemical, or carbon dioxide
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.88 ppm
2. Eye irritation level: 75 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, cyclohexanone can be detected at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cyclohexanone is 50 parts of cyclohexanone per million parts of air (ppm) [200 milligrams of cyclohexanone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 25 ppm (100 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 25 ppm (100 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for cyclohexanone

	Exposure limits ppm	Exposure limits mg/m³
OSHA PEL TWA	50	200
NIOSH REL TWA	25	100
ACGIH TLV® TWA (Skin)	25	100

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Subchronic inhalation of cyclohexanone by rabbits and monkeys caused central nervous system depression and liver and kidney degeneration. Cutaneous or subcutaneous application of cyclohexanone for several days caused cataracts in guinea pigs.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cyclohexanone can cause dizziness and unconsciousness. Irritation of the eyes, nose, and throat can also occur.
2. *Long-term (chronic):* Dermal exposure to cyclohexanone can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cyclohexanone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cyclohexanone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindication to job placement, include concurrent dermatitis or a history of chronic skin disease.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to cyclohexanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to cyclohexanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting cyclohexanone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cyclohexanone may also be used if available. A detailed sampling and analytical method for cyclohexanone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with cyclohexanone.

Workers should be provided with and required to use splash-proof safety goggles where cyclohexanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cyclohexanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cyclohexanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cyclohexanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cyclohexanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cyclohexanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cyclohexanone

Operations	Controls
During surface coating or spray painting of fabrics and plastics	Local exhaust ventilation, personal protective equipment
During cleaning of leathers and textiles; during degreasing of leathers and metals	Local exhaust ventilation, personal protective equipment
During use as a solvent in crude rubber, insecticides, and epoxy resins; during use as a sludge solvent in lubricating oils	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cyclohexanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If cyclohexanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to cyclohexanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cyclohexanone gets on the skin, wash it immediately with soap and water. If cyclohexanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cyclohexanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cyclohexanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place (such as a fume hood) for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cyclohexanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cyclohexanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cyclohexanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Cyclohexanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cyclohexanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 625 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 1,250 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 5,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 5,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 25 ppm (100 mg/m^3) (TWA).

Occupational Health Guideline for Cyclohexene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_{10}
- Synonyms: Benzene tetrahydride
- Appearance and odor: Colorless liquid with a sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclohexene is 300 parts of cyclohexene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1015 milligrams of cyclohexene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to cyclohexene may cause irritation of the eyes, nose, and throat.

2. Long-term Exposure: Prolonged or repeated contact of this chemical with the skin may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclohexene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclohexene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclohexene exposure.

—Skin disease: Cyclohexene can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although cyclohexene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although cyclohexene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexene might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

While no significant toxicologic studies on cyclohexene have been reported, it is regarded as a mild respiratory irritant and central nervous system depressant, chiefly by analogy to the observed effect of chemically similar substances. No acute or chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 82
2. Boiling point (760 mm Hg): 82.8 C (181 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of cyclo-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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hexene): 2.8

5. Melting point: −103.7 C (−155 F)

6. Vapor pressure at 20 C (68 F): 67 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Very low

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexene.

4. Special precautions: Cyclohexene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −12 C (10 F) (closed cup)

2. Autoignition temperature: 310 C (590 F)

3. Flammable limits in air, % by volume: Lower: 1.2; Upper: 4.8 at 100 C (212 F)

4. Extinguishant: Dry chemical, carbon dioxide, foam

- **Warning properties**

1. Odor Threshold: By analogy to cyclohexane, which has an odor threshold of 0.41 ppm according to May, the odor of cyclohexene is assumed to be below the permissible exposure limit of 300 ppm.

2. Eye Irritation Level: The *Documentation of TLV's* states that "Cook suggested 400 ppm as a TLV (for cyclohexene) on the basis of analogy to cyclohexane. This limit has subsequently been reduced to 300 ppm to provide a wider margin of safety from systemic effects and to reduce irritation."

3. Evaluation of Warning Properties: By analogy to cyclohexane, the odor threshold of cyclohexene is assumed to be below the permissible exposure limit. Cyclohexene, therefore, is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cyclohexene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cyclohexene may be used. An analytical method for cyclohexene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cyclohexene.
- Clothing wet with liquid cyclohexene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclohexene, the person performing the operation should be informed of cyclohexene's hazardous properties.
- Any clothing which becomes wet with liquid cyclohexene should be removed immediately and not reworn until the cyclohexene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid cyclohexene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid cyclohexene should be promptly washed or showered with soap or mild detergent and water to remove any cyclohexene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclohexene may occur and control methods which may be effective in each case:

Operation	Controls
Use in organic synthesis as a starting material or chemical intermediate	Process enclosure; local exhaust ventilation; personal protective equipment; general dilution ventilation
Use as a constituent to study catalytic reactions, mechanisms of oxidation of hydrocarbons, and reaction kinetics	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in synthesis of polymers; as a polymer modifier to control molecular weight; use as a stabilizing agent	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during catalytic hydrogenation of aromatic compounds	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cyclohexene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If cyclohexene gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If cyclohexene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of cyclohexene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If cyclohexene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If cyclohexene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Cyclohexene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Cyclohexene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR CYCLOHEXENE

Condition	**Minimum Respiratory Protection* Required Above 300 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND GUIDELINE FOR CYCLOHEXYLAMINE

INTRODUCTION

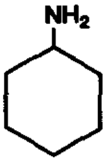
This guideline summarizes pertinent information about cyclohexylamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NH_2$

- **Structure**



- **Synonyms**

Aminocyclohexane, aminohexahydrobenzene, CHA, cyclohexanamine, hexahydroaniline, hexahydrobenzenamine

- **Identifiers**

1. CAS No.: 108-91-8
2. RTECS No.: GX0700000
3. DOT UN: 2357 68
4. DOT label: Flammable liquid; corrosive

- **Appearance and odor**

Cyclohexylamine is a flammable, colorless or yellow liquid with a strong, fishy, amine odor. The odor threshold of cyclohexylamine is 2.6 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 99.17
2. Boiling point (760 mm Hg): 134.5°C (274.1°F)
3. Specific gravity (water = 1): 0.87 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of cyclohexylamine): 3.42
5. Melting point: -17.7°C (0.14°F)

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 11.3 mm Hg

7. Solubility: Completely soluble in water and most organic solvents, including alcohols, ethers, ketones, esters, and chlorinated hydrocarbons; also soluble in peanut oil, mineral oil, acetone, and benzene.

8. Evaporation rate (ether = 1): 82.9

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. Contact of the vapor with air generates an explosive mixture.

2. Incompatibilities: Contact of cyclohexylamine with oxidizers, organic compounds, acid anhydrides, acid chlorides, alkylene oxides, acids, any copper alloy, zinc, or galvanized steel may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving cyclohexylamine.

4. Special precautions: Avoid contact of the vapors with air.

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to cyclohexylamine.

1. Flash point: 31°C (88°F) (open cup)

2. Autoignition temperature: 293°C (560°F)

3. Flammable limits in air (% by volume): Lower 1.5; upper 9.4

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving cyclohexylamine. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving cyclohexylamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cyclohexylamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclohexylamine. Structural firefighters' protective clothing may provide limited protection against fires involving cyclohexylamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclohexylamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (40 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclohexylamine a threshold limit value (TLV) of 10 ppm (41 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of severe eye and skin irritation associated with exposure to cyclohexylamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclohexylamine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cyclohexylamine is a severe irritant of the eyes, mucous membranes, and skin in animals. A single drop of a 50% aqueous solution of cyclohexylamine onto the conjunctival sac of a rabbit's eye caused complete destruction of the eye [ACGIH 1991]. When applied to the skin of rabbits, this substance caused severe skin damage [NIOSH 1990]. Although skin sensitization tests in guinea pigs yielded negative results, cyclohexylamine is believed to have weak sensitizing potential [ACGIH 1991; NJDH 1991]. The dermal LD_{50} in rabbits is 277 mg/kg [NIOSH 1990]. Fifty percent of exposed rats died after inhaling a cyclohexylamine concentration of 7,500 mg/m^3 for an unspecified time [NIOSH 1990]. Acutely poisoned animals displayed signs of severe irritation and of central nervous system effects before death [NIOSH 1990]. Rabbits, rats, and guinea pigs exposed for 7 hr/day, 5 days/week to a 1,200-ppm concentration of cyclohexylamine died after a single exposure; however, most animals exposed to a 150-ppm concentration on the same regimen survived for 10 such exposures. Before death, animals of all species exhibited signs of eye and respiratory tract irritation and developed corneal opacities [Clayton and Clayton 1981]. The oral LD_{50} is 156 mg/kg for rats and 224 mg/kg for mice [NIOSH 1990]. In rats, cyclohexylamine has caused reproductive effects in males (reduction in the number and size of litters sired) and females (reduction in pregnancy rate, number of live-born fetuses and post-natal survivors, and birthweight of offspring) [Clayton and Clayton 1981]. In experiments involving rats, mice, and dogs, cyclohexylamine has induced fetotoxic and/or paternal reproductive effects by oral, intraperitoneal, and parenteral administration [NIOSH 1990]. Cyclohexylamine has caused chromosomal breaks in a number of in-vitro test systems [IARC 1980]. Cyclohexylamine has been tested for carcinogenicity in two oral bioassays in mice and four in rats. Based on the results of this research, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of cyclohexylamine in animals is inadequate [IARC 1980].
2. *Effects on Humans:* Cyclohexylamine is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans; it may also cause skin sensitization in some individuals. Cyclohexylamine has caused severe irritation upon contact with the skin; patch tests have shown that this substance is capable of causing skin sensitization [NIOSH 1990; Clayton and Clayton 1981]. Three workers who had been accidentally overexposed to an unspecified concentration of cyclohexylamine experienced symptoms of lightheadedness, drowsiness, anxiety, apprehension, and nausea; one acutely poisoned worker also developed slurred speech and vomited [Hathaway et al. 1991]. Human volunteers who ingested 5 grams of cyclohexylamine a day for 7 or 8 consecutive days showed no adverse effects; workers exposed to airborne concentrations of this substance in the range of 4 to 10 ppm also reported experiencing no symptoms [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyclohexylamine can cause severe irritation of the eyes, with tearing and conjunctivitis; irritation of the respiratory tract, with coughing and difficult breathing; and severe skin irritation, with burns, blisters, redness, swelling, and cell death. Acutely poisoned workers also may experience apprehension, drowsiness, lightheadedness, and vomiting.

2. *Chronic exposure:* Repeated or chronic exposure to cyclohexylamine may cause corneal opacities, dryness and cracking of the skin, and, in some individuals, skin sensitization, with itching, wheals, and redness of the affected areas.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of cyclohexylamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclohexylamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclohexylamine and may result in worker exposures to this substance:

—Use as an intermediate in the production of cyclamate sweeteners and textile and rubber chemicals

—Use as a corrosion inhibitor in boiler feed water and oil fields and in the packaging of metal equipment

—Manufacture of dyes, insecticides, plasticizers, emulsifying agents, acid gas absorbents, and dry-cleaning soaps

The following methods are effective in controlling worker exposures to cyclohexylamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyclohexylamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society (ATS) [1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclohexylamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclohexylamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclohexylamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclohexylamine.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclohexylamine is determined by using a silica gel tube (600/150/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 96 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in Method P&CAM 221 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If cyclohexylamine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyclohexylamine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyclohexylamine, particularly its potential to cause severe irritation of the eyes and skin.

A worker who handles cyclohexylamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclohexylamine or a solution containing cyclohexylamine is handled, processed, or stored.

STORAGE

Cyclohexylamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclohexylamine should be protected from physical damage and should be stored separately from strong oxidizers (such as chlorine, bromine, and fluorine), acids, copper alloys, lead, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle cyclohexylamine. To prevent static sparks, containers and equipment should be grounded and bonded for transfers. Because containers that formerly contained cyclohexylamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyclohexylamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the cyclohexylamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of cyclohexylamine must comply with EPA's emergency planning requirements [40 CFR Part 355.30].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for cyclohexylamine is 1 or more lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyclohexylamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cyclohexylamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclohexylamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, or gauntlets, as appropriate) should be worn to prevent any skin contact with cyclohexylamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have breakthrough times of less than 1 hr and are not recommended for use with cyclohexylamine: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl alcohol, polyvinyl chloride, and Viton.

If cyclohexylamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclohexylamine might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclohexylamine. Contact lenses should not be worn if the potential exists for cyclohexylamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLONITE

INTRODUCTION

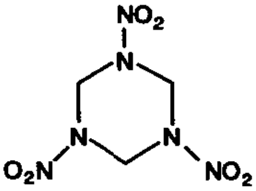
This guideline summarizes pertinent information about cyclonite for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_6N_6O_6$

- **Structure**



- **Synonyms**

RDX; trimethylene trinitramine; cyclotrimethylenenitramine; cyclotrimethylenetrinitramine; hexahydro-1,3,5-trinitro-s-triazine; Hexogen 5W; Hexolite; PBX(AF) 108; sym-trimethylenetrinitramine; trinitrocyclotrimethylene triamine; 1,3,5-trinitro-1,3,5-triazacyclohexane

- **Identifiers**

1. CAS No.: 121-82-4
2. RTECS No.: XY9450000
3. DOT UN: 0072 (wetted with not <25% water, by weight, or desensitized with not <10% phlegmatizer, by weight); 0072 (wetted with not <15 percent water, by weight); 0483 (desensitized)
4. DOT label: Explosive A, corrosive

- **Appearance and odor**

Cyclonite is a white, crystalline powder that is a powerful high explosive. It is also used occasionally as a rodenticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.26
2. Boiling point: Data not available
3. Specific gravity (water = 1): 1.82 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 205° to 206°C (401° to 402.8°F)
6. Vapor pressure: 0.0004 mm Hg at 110°C (230°F)
7. Solubility: Insoluble in water, alcohol, benzene, car-

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bon tetrachloride, and carbon disulfide; slightly soluble in ethyl acetate, methanol, ether, and toluene; soluble in acetone

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Shock or heat

2. Incompatibilities: Contact with mercury fulminate detonates cyclonite, and contact with combustibles or strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases (such as the oxides of nitrogen) may be released in a fire involving cyclonite.

4. Special precautions: Cyclonite is one of the most powerful explosives in use today. It must be stored in an explosives magazine and be handled accordingly.

Flammability

The National Fire Protection Association has not assigned a flammability rating to cyclonite; however, this substance is a dangerous explosion hazard.

1. Flash point: Explodes

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Evacuate the area if cyclonite or materials in the vicinity of cyclonite catch fire. This material is a high explosive and must be handled accordingly. The Fire Department should be called immediately if cyclonite is on fire or materials near this substance catch fire.

Fires involving cyclonite should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclonite.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclonite [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1.5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 3 mg/m^3 as a short-term exposure limit (STEL), both with a "Skin" notation. A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclonite a threshold limit value (TLV) of 1.5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to cyclonite [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of central nervous system effects associated with exposure to cyclonite.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclonite can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cyclonite is toxic to the central nervous system. The oral LD$_{50}$s in the rat and mouse are 100 mg/kg and 59 mg/kg, respectively; before death, these animals lost weight, became increasingly irritable, and had frequent convulsions. At autopsy, the animals showed lung and gastrointestinal tract congestion [NIOSH 1993; Clayton and Clayton 1981]. Others report an oral LD$_{50}$ of approximately 200 mg/kg in rats [ACGIH 1991]. Seven dogs given 50 mg cyclonite/day, 6 days/week for 6 weeks showed no blood changes and did not develop methemoglobinemia; however, they became excited and irritable, had hyperactive reflexes, and convulsed and collapsed within 1 week of the onset of dosing. At autopsy, no microscopic pathology was seen [Clayton and Clayton 1981; ACGIH 1991]. The low-

est oral dose of cyclonite reported to cause developmental toxicity in the rat is 3 g/kg; 20 mg/kg cyclonite administered on days 6 to 15 of gestation caused fetotoxicity [NIOSH 1993].

2. *Effects on Humans:* In humans, cyclonite is toxic to the central nervous system. Epileptiform seizures have occurred either without warning or after a few days of insomnia, restlessness, and irritability in workers manufacturing cyclonite explosives. The seizures were most frequent in persons inhaling cyclonite-laden dust; the postconvulsive interval was characterized by temporary amnesia, malaise, fatigue, and weakness, but recovery was eventually complete [Clayton and Clayton 1981; ACGIH 1991]. Workers in a large cyclonite manufacturing plant who handled the material in the moist state did not convulse or show other signs of cyclonite poisoning, but they did develop primary irritant and sensitization dermatitis, particularly of the face and eyelids; these skin conditions are believed to have been caused by unidentified intermediates used in the manufacturing process. Patch tests confirmed that cyclonite had not caused the irritation [Clayton and Clayton 1981]. Five workers convulsed or lost consciousness after handling cyclonite in a dusty atmosphere. These workers developed headaches, nausea, vomiting, or unconsciousness either at work or later at home; unconsciousness lasted several minutes to 24 hr and was accompanied by varying degrees of stupor, nausea, vomiting, and weakness. The workers recovered completely, but two of the men became ill again when they were re-exposed to cyclonite [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to cyclonite include headache; irritability; fatigue; weakness; tremors; nausea; dizziness; vomiting; insomnia; unconsciousness; and seizures.

2. *Chronic exposure:* Continued low-level exposure to cyclonite can cause irritability, sleeplessness, and seizures. Cyclonite may cause skin sensitization; if sensitization occurs, very low future exposures can cause itching, the development of a skin rash, and hives.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of cyclonite. Cyclonite can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclonite or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclonite and result in worker exposures to this substance:

—Manufacture, handling, and use of cyclonite explosives, munitions, and solid propellants

—Manufacture, formulation, and application of cyclonite-containing rodenticides

The following methods are effective in controlling worker exposures to cyclonite, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyclonite, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclonite at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or findings consistent with diseases of the central nervous system or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclonite exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclonite on the central nervous system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclonite.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclonite is determined by using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cyclonite contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cyclonite should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyclonite.

A worker who handles cyclonite should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclonite or a solution containing cyclonite is handled, processed, or stored.

STORAGE

Cyclonite should be stored in a permanent explosives magazine. Detached storage is required. Containers of cyclonite should be protected from shock, friction, and physical damage and should be separated from initiator explosives, strong oxidizers, combustibles, shock, heat, sparks, and open flame. Because containers that formerly contained cyclonite may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cyclonite, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill.

5. Use nonsparking tools for cleanup.

6. Cover the spill with soda ash and spray the area with water. Use a shovel to place the spilled material into a closed container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Cyclonite is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cyclonite; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyclonite emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although cyclonite is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclonite exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cyclonite. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyclonite permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyclonite.

If cyclonite is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclonite might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclonite. Contact lenses should not be worn if the potential exists for cyclonite exposure.

REFERENCES CITED

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NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

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Occupational Health Guideline for Cyclopentadiene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_5H_6
- Synonyms: 1,3-Cyclopentadiene
- Appearance and odor: Colorless liquid with a sweet odor like turpentine; dimer is a crystalline material with a camphor-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclopentadiene is 75 parts of cyclopentadiene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 200 milligrams of cyclopentadiene per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclopentadiene might possibly affect the body if it is inhaled, is swallowed, or allowed to come in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to cyclopentadiene may cause irritation of the eyes and nose.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclopentadiene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclopentadiene at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclopentadiene exposure.

—Liver disease: Although cyclopentadiene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although cyclopentadiene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclopentadiene might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Cyclopentadiene vapor is irritating to the eyes and nose and has an objectionable odor. Repeated daily exposure of rats at 500 ppm produced mild toxic effects in the liver and kidneys, whereas repeated daily exposures in several species of animals at 250 ppm for 135 times produced no manifest effects. Dogs exposed to repeated daily exposures of up to 800 ppm had no ill effects; liver function and hematologic findings remained negative. Chronic systemic effects have not been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 66
  2. Boiling point (760 mm Hg): 41.5 C (107 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of cyclo-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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pentadiene): 2.3

5. Melting point: −85 C (−121 F)

6. Vapor pressure at 20 C (68 F): Data not available

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat. Cyclopentadiene is converted to the higher boiling dicyclopentadiene on storage even at 0 C (32 F). The reaction may become violent at higher temperatures.

2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclopentadiene.

4. Special precautions: Cyclopentadiene should be stored at −20 to 0 C (−4 F to 32 F). When stored in bulk, the conversion to dicyclopentadiene may become violent if the temperature is allowed to rise above 0 C (32 F).

- **Flammability**

1. Flash point: Less than 32 C (90 F) (open cup) (flash point of dimer)

2. Autoignition temperature: 640 C (1184 F)

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Dry chemical, carbon dioxide, foam

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, cyclopentadiene has "an irritating, terpene-like odor," but no quantitative information is available concerning its odor threshold.

The *Documentation of TLV's* states that "human sensory response was distinctly unfavorable at both 500 ppm and 250 ppm. Thus, although systemic injury is not to be expected from exposure concentrations averaging 250 ppm, a concentration significantly below 250 ppm is required from the standpoint of comfort. A TLV of 75 ppm is recommended."

2. Eye Irritation Level: Cyclopentadiene vapor is not specifically known to cause eye irritation. Grant states that "a less reactive cyclopentadiene-dimer formed by spontaneous polymerization has been tested on rabbit eyes and found to be only slightly injurious . . . ."

3. Evaluation of Warning Properties: Through its sensory effects, cyclopentadiene can be detected at a concentration of about 3 times the permissible exposure limit. For the purposes of this guideline, therefore, cyclopentadiene is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for cyclopentadiene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cyclopentadiene.
- Clothing wet with liquid cyclopentadiene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclopentadiene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclopentadiene, the person performing the operation should be informed of cyclopentadiene's hazardous properties.
- Any clothing which becomes wet with liquid cyclopentadiene should be removed immediately and not reworn until the cyclopentadiene is removed from the

clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid cyclopentadiene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid cyclopentadiene should be promptly washed or showered with soap or mild detergent and water to remove any cyclopentadiene.
- Employees who handle liquid cyclopentadiene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclopentadiene may occur and control methods which may be effective in each case:

Operation	Controls
Use in thermal cracking of dicyclopentadiene; use in chemical synthesis	General dilution ventilation; personal protective equipment
Use in production of modified oil similar to tung oil from linseed or soybean oil	General dilution ventilation; personal protective equipment
Use in preparation of epoxy resins; preparation of ladder polymers; preparation of varnishes; use as a drying oil for varnishes	General dilution ventilation; personal protective equipment
Use in production of fire-resistant polyurethane foams; production of heat-stable, fire-resistant laminating agents and surface coatings; production of sanitary can coatings	General dilution ventilation; personal protective equipment
Use in production of foundry-core bindings; production of epoxidized olefins	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cyclopentadiene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If cyclopentadiene gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If cyclopentadiene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent.

- **Breathing**

If a person breathes in large amounts of cyclopentadiene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If cyclopentadiene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If cyclopentadiene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, allow the material to dimerize, collect on paper or other material. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities may be reclaimed or dissolved in an appropriate solvent and atomized in a suitable combustion chamber. Cyclopentadiene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Cyclopentadiene may disposed of by dissolving in an appropriate solvent and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR CYCLOPENTADIENE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
750 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLOPENTANE

INTRODUCTION

This guideline summarizes pertinent information about cyclopentane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_5H_{10}

- **Synonyms**

  Pentamethylene

- **Identifiers**

  1. CAS No.: 287-92-3
  2. RTECS No.: GY2390000
  3. DOT UN: 1146 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Cyclopentane is a flammable, mobile, colorless liquid with a mild, sweet odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 70.13
  2. Boiling point (760 mm Hg): 49.3°C (120.7°F)
  3. Specific gravity (water = 1): 0.75 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyclopentane): 2.42
  5. Melting point: -94°C (-137.2°F)
  6. Vapor pressure at 31°C (87.8°F): 400 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, acetone, benzene, petroleum ether, carbon tetrachloride.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame

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2. Incompatibilities: Contact of cyclopentane with strong oxidizing agents (such as chlorine, bromine, or fluorine) may cause a reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving cyclopentane.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to cyclopentane.

1. Flash point: -37°C (-35°F) (closed cup)

2. Autoignition temperature: 361°C (682°F)

3. Flammable limits in air (% by volume): Lower, 1.1; upper, 8.7

4. Extinguishant: Use dry chemical, standard foam, or carbon dioxide to fight fires involving cyclopentane. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving cyclopentane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cyclopentane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclopentane. Structural firefighters' protective clothing may provide limited protection against fires involving cyclopentane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclopentane [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 600 ppm (1,720 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for cyclopentane [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclopentane a threshold limit value (TLV) of 600 ppm (1,720 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the risk of CNS depression and skin irritation associated with cyclopentane exposure. The ACGIH limit is based on the risk of narcotic effects associated with exposure to cyclopentane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclopentane can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Cyclopentane is a central nervous system depressant in animals. Application of cyclopentane to the skin of guinea pigs caused redness and dryness [Clayton and Clayton 1981]. The minimal narcotic concentration in mice is 38.3 ppm; this level of exposure may also cause loss of reflexes and death. The margin of safety between the minimal narcotic dose and the lethal dose is thus very small [Clayton and Clayton 1981]. Exposure to a cyclopentane concentration of 112 to 1,139 ppm for 6 hours/day for 3 weeks caused no effects in male and

female rats; however, exposure to 8,110 ppm for 6 hours/day for 12 weeks caused a decrease in the rate of body weight gain in female rats [Clayton and Clayton 1981].

2. *Effects on Humans:* Cyclopentane is a central nervous system depressant in humans. Because the industrial use of pure cyclopentane is limited and the commercial reagents and solvents that contain cyclopentane also contain other hydrocarbons, there are few toxicologic data on the effects of exposure to the pure substance [ACGIH 1991]. Prolonged contact of this substance with the skin may produce dryness and cracking [NJDH 1989]. Exposure to a 10 to 15 ppm concentration of cyclopentane for an unspecified period is reported to have been tolerated by volunteers [Clayton and Clayton 1981]. The central nervous system effects of exposure to cyclopentane include lightheadedness, dizziness, excitement, incoordination, nausea, vomiting, loss of consciousness, and, if exposure is severe, death due to respiratory failure [Sittig 1985]. One hundred twenty-two Italian shoe factory workers exposed for unspecified periods to unidentified concentrations of glue solvents that contained both cyclopentane and n-hexane developed polyneuropathy; however, the extent to which these polyneuropathies were attributable to cyclopentane exposure is unclear [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to cyclopentane may include lightheadedness, dizziness, excitement, incoordination, nausea, vomiting, stupor, loss of consciousness, and death. Contact with cyclopentane can irritate the skin and eyes.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to cyclopentane include dryness and cracking of the skin. Although cyclopentane has not been adequately evaluated for the possibility of brain and nerve damage following repeated exposures, other solvents and petroleum-based chemicals have been shown to cause such damage, including: reduced memory and concentration, fatigue, sleep disturbances, and reduced coordination.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of cyclopentane. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclopentane or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclopentane and lead to worker exposures to this substance:

—Use in cracking of aromatics

—Use as an intermediate in the production of various chemicals and pharmaceuticals, including analgesics, sedatives, hypnotics, antitumor agents, prostaglandins, depressants, and insecticides

—Use as a component of solvents used for cellulose ethers, motor fuels, and as an azeotropic distillation agent

—Use in the production of cyclopentadiene

—Use as a laboratory chemical

The following methods are effective in controlling worker exposures to cyclopentane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyclopentane, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclopentane at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclopentane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclopentane on the skin and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclopentane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne cyclopentane is made using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 5 liters is collected. The sample is then treated with carbon disulfide to extract the cyclopentane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If cyclopentane contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with cyclopentane should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of cyclopentane.

A worker who handles cyclopentane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclopentane or a solution containing cyclopentane is handled, processed, or stored.

STORAGE

Cyclopentane should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must meet OSHA requirements for Class IB flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclopentane should be protected from physical damage and should be stored separately from strong oxidizing agents (such as chlorine, bromine, and fluorine), heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters. Only nonsparking tools may be used to handle cyclopentane. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained cyclopentane may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyclopentane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the cyclopentane for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyclopentane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cyclopentane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of cyclopentane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although cyclopentane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclopentane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cyclopentane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber and natural rubber have been tested against permeation by cyclopentane and have breakthrough times of less than one hour; therefore, they are not recommended for use with cyclopentane. No other reports were found on the resistance of additional protective clothing materials to cyclopentane permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyclopentane.

If cyclopentane is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclopentane might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclopentane. Contact lenses should not be worn if the potential exists for cyclopentane exposure.

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Occupational Health Guideline for
2,4-D*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cl_2C_6H_3OCH_2COOH$
- Synonyms: 2,4-Dichlorophenoxyacetic acid
- Appearance and odor: Colorless, odorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2,4-D is 10 milligrams of 2,4-D per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2,4-D can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Massive exposure to 2,4-D may cause weakness, stupor, muscle twitching, and convulsions. Contact of the material with the skin may cause a rash. It has caused minor liver and kidney damage in animals.

2. Long-term Exposure: Not known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2,4-D.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2,4-D at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 2,4-D exposure.

—Liver disease: 2,4-D causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 2,4-D causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: 2,4-D causes ventricular fibrillation in animals. In persons with impaired cardiovascular function, the inhalation of 2,4-D might cause exacerbation of pre-existing disorder.

—Skin disease: 2,4-D can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Convulsive disorder or neuropathy: 2,4-D may cause convulsions in humans. Persons with a history of such disorders may be more susceptible to the effects of this agent. 2,4-D may also produce neuropathy by analogy to effects observed in experimental animals.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

2,4-D dust causes signs of both hypo- and hyperexcitation of the central nervous system in animals. In several species of animals given massive oral doses, sudden death has been ascribed to ventricular fibrillation. If death is delayed, myotonia, stiffness of the extremities, ataxia, paralysis, and coma are seen; autopsy findings have included minor liver and kidney injury. The myotonia characteristic of intoxication by 2,4-D in animals has not been reported in humans. Possibly the only recognized fatal case of poisoning involved a suicidal person who ingested not less than 6500 mg; the

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person apparently experienced violent convulsions, although they were not actually observed; there were no significant findings at autopsy. A single dose of 3.6 g of 2,4-D administered intravenously to a patient for treatment of disseminated coccidiomycosis caused stupor, hyporeflexia, fibrillary twitching of some muscles, and urinary incontinence; 24 hours after the dose, the patient still complained of profound muscular weakness, which subsided after an additional 24 hours. Contact of the material with the skin may cause dermatitis; skin absorption is slight.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 221
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.1 (estimated)
  4. Vapor density (air = 1 at boiling point of 2,4-D): 7.63
  5. Melting point: 140 C (284 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, at 20 C (68 F): 0.07 ppm
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving 2,4-D.
  4. Special precautions: None
- **Flammability**
  1. Flash point: Data not available
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Carbon dioxide, dry chemical, foam, water
- **Warning properties**

Since 2,4-D has a negligible vapor pressure, warning properties are not considered.

Grant states that "2,4-dichlorophenoxyacetic acid (2,4-D) is a herbicide for weed control, often used in the form of its salts or esters. Parenteral administration to dogs has caused sneezing, lacrimation, and rubbing of the eyes, along with gastrointestinal disturbances. In three human beings, absorption of an unspecified ester of dichlorophenoxyacetic acid through the skin caused polyneuritis, but with no disturbance of the eyes or vision." The above do not appear to be local effects on the eye. However, Stolman and Stecher note that this substance can cause irritation of the eyes.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 2,4-D is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with 2,4-D or liquids containing 2,4-D.
- If employees' clothing may have become contaminated with 2,4-D, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with 2,4-D should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2,4-D from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2,4-D, the person performing the operation should be informed of 2,4-D's hazardous properties.
- Non-impervious clothing which becomes contami-

nated with 2,4-D should be removed promptly and not reworn until the 2,4-D is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where 2,4-D or liquids containing 2,4-D may contact the eyes.

SANITATION

- Skin that becomes contaminated with 2,4-D should be promptly washed or showered with soap or mild detergent and water to remove any 2,4-D.
- Eating and smoking should not be permitted in areas where solid 2,4-D is handled, processed, or stored.
- Employees who handle 2,4-D or liquids containing 2,4-D should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2,4-D may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of herbicides	Process enclosure; local exhaust ventilation; personal protective equipment; washing facilities
Manufacture of 2,4-D	Process enclosure; local exhaust ventilation; personal protective equipment; washing facilities
Application on cereal crops, corn, sorghum, milo, sugar cane, pastures, range land, and lawns for use as an herbicide; use as a plant hormone on agricultural crops	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 2,4-D or liquids containing 2,4-D get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 2,4-D or liquids containing 2,4-D get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 2,4-D or liquids containing 2,4-D penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 2,4-D, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 2,4-D has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If 2,4-D is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dispose of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device, as in below or deposit in a secured sanitary landfill.

- Waste disposal methods:

2,4-D may be disposed of:

1. By making packages of 2,4-D in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving 2,4-D in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By disposal in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR 2,4-D

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
100 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
500 mg/m³ or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s), and dust filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR

DDT

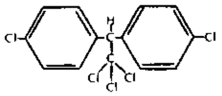
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about DDT for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{14}H_9Cl_5$
- **Structure:**



- **Synonyms:** Citox; genitox; dichlorodiphenyltrichloroethane; 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
- **Identifiers:** CAS 50-29-3; RTECS KJ3325000; DOT 2761
- **Appearance and odor:** Colorless crystals or white to slightly off-white powder with a slightly aromatic odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 354.48
2. Boiling point (at 760 mmHg): 260°C (500°F)
3. Specific gravity (water = 1): 1.56
4. Vapor density (air = 1 at boiling point of DDT): 12.2
5. Melting point: 105-109°C (221-228°F)
6. Vapor pressure at 20°C (68°F): 1.5×10^{-7} mmHg
7. Practically insoluble in water

- **Reactivity**

1. Incompatibilities: DDT should not be stored in iron containers; DDT should not be mixed with iron and aluminum salts or with alkaline materials. Temperatures greater than 100°C (212°F) may cause decomposition.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride) may be released in a fire involving DDT.
3. Caution: DDT should be stored in a tightly closed container in a well-ventilated area.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DDT is 1 milligram of DDT per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that DDT be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.5 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 1 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek; the short-term exposure limit (STEL) is 3 mg/m^3 (Table 1).

Table 1.—Occupational exposure limits for DDT

	Exposure limits mg/m^3
OSHA PEL TWA (Skin)*	1
NIOSH REL TWA (CA)†	0.5§
ACGIH TLV® TWA	1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ Lowest reliably detectable level.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

NOTE: A general ban was ordered by the Environmental Protection Agency on the registration of DDT, effective December 31, 1972. Effective the same date, the ban for uses of DDT by public health officials in disease control programs and by USDA and the military for health quarantine and prescription drugs use was lifted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

DDT may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute oral administration of DDT to rats caused tissue destruction (necrosis) of the liver, mild degeneration of kidney tubules, and changes in electroencephalograms. Chronic oral administration of DDT caused decreased fertility in rats and increased mortality of their offspring, toxic effects on the liver (including necrosis, fat deposition, increased weight, and increased enzyme activity), and liver cancer. In mice, chronic oral administration of DDT produced cancers of the liver, lungs, and lymphatic system.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to DDT can cause a prickling sensation of the tongue, lips, and face, a general feeling of ill health, headache, fatigue, vomiting, dizziness, tremors, convulsions, partial paralysis of the hands, and coma. DDT can also cause irritation of the eyes and skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to DDT, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic or laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, and reproductive and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DDT at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic liver disease. Workers should inform their physicians of their potential for exposures to DDT because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter."

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DDT. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, and reproductive and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DDT may cause adverse reproductive effects or diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to DDT should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• Method

Sampling and analysis may be performed by collecting DDT vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure DDT may also be used if available. A detailed sampling and analytical method for DDT may be found in the *NIOSH Manual of Analytical Methods* (method number S 274).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with DDT.

SANITATION

Clothing which is contaminated with DDT should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DDT from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DDT's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with DDT should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DDT should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DDT may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for DDT

Operations	Controls
During preparation and handling of insecticide	Process enclosure, local exhaust ventilation, personal protective equipment
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to DDT, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DDT gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to DDT, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DDT gets on the skin, wash it immediately with soap and water. If DDT penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DDT is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing DDT, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing DDT may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. If in solid form, DDT may be collected and placed in an appropriate container.
5. DDT dust may be collected by vacuuming with an appropriate high-efficiency filtration system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for DDT

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DECABORANE

INTRODUCTION

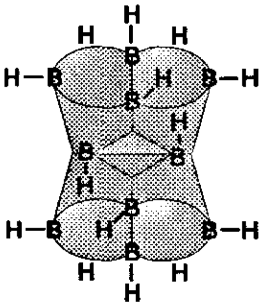
This guideline summarizes pertinent information about decaborane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$B_{10}H_{14}$

- **Structure**



- **Synonyms**

Decaboron tetradecahydride, boron hydride

- **Identifiers**

1. CAS No.: 17702-41-9
2. RTECS No.: HD1400000
3. DOT UN: 1868 34
4. DOT label: Flammable solid, poison

- **Appearance and odor**

Decaborane is a colorless to white crystalline solid with a bitter, chocolate-like odor. The median odor threshold for decaborane is 0.06 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 122.3
2. Boiling point (760 mm Hg): 213°C (416°F)
3. Specific gravity (water = 1): 0.94 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of decaborane): 4.2
5. Melting point: 99.7°C (211°F)
6. Vapor pressure at 25°C (77°F): 0.05 mm Hg
7. Solubility: Slightly soluble in cold water; soluble in

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
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benzene, hexane, toluene, alcohol, and ether; very soluble in carbon disulfide

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Contact of decaborane with oxidizers, oxygenated solvents, or dimethyl sulfoxide causes fires or explosions. In contact with carbon tetrachloride, ethers, or halocarbons, decaborane forms impact-sensitive mixtures.
3. Hazardous decomposition products: Toxic fumes (such as boron oxides) may be released in a fire involving decaborane.
4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to decaborane.

1. Flash point: 80°C (176°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, waterspray, or regular foam to fight fires involving decaborane.

Fires involving decaborane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of decaborane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving decaborane. Structural firefighters' protective clothing may provide limited protection against fires involving decaborane.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for decaborane is 0.05 ppm (0.3 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.3 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and a STEL of 0.15 (0.9 mg/m^3). A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day. The NIOSH REL and STEL also bear a "Skin" notation [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned decaborane a threshold limit value (TLV) of 0.05 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm for periods not to exceed 15 minutes. The ACGIH also assigns decaborane a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The OSHA, NIOSH, and ACGIH limits are based on the risk of neuropathic, hepatic, and nephrotoxic effects associated with exposure to decaborane [54 Fed. Reg. 2409; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to decaborane can occur through inhalation, ingestion, eye and skin contact, and absorption through the skin.

- **Summary of toxicology**

  1. *Effects on Animals:* Decaborane is toxic to the central nervous system, liver, cardiovascular system, and kidneys of experimental animals. It is toxic by all routes of exposure, and cumulative effects have been reported in rats, rabbits, and dogs [Clayton and Clayton 1981; Parmeggiani 1983]. Corneal opacities developed in mice and rats following a 4-hr exposure to a 26-ppm concentration of decaborane [Hathaway et al. 1991]. The dermal LD_{50} is 71 mg/kg in rabbits and 740 mg/kg in rats [NIOSH 1993]. The 4-hr LC_{50} is 46 ppm in rats and 12 ppm in mice [NIOSH 1993]. The oral LD_{50} is 64 mg/kg in rats and 41 mg/kg in mice [NIOSH 1993]. The manifestations of acute decaborane-induced central nervous system toxicity in rodents include hyperexcitability, restlessness, coarse head movements, generalized weakness, rigid hindquarters, absent eye reflexes, convulsive seizures, depressed breathing, and narcosis [Parmeggiani 1983; Hathaway et al. 1991]. Repeated low-dose oral exposure (3 mg/kg) to decaborane did not cause marked central nervous system effects in any test species but did cause liver and kidney damage [Hathaway et al. 1991]. Cardiovascular toxicity is manifested in dogs as slow heart rate, initial moderate elevation in blood pressure, and a final drop in blood pressure after lethal doses of decaborane are administered by any route [Hathaway et al. 1991; Parmeggiani 1983].

  2. *Effects on Humans:* Decaborane causes central nervous system effects in humans. Exposure causes headaches, dizziness, drowsiness, and nausea, and severe exposure is expected to cause general weakness, incoordination, hyperexcitability, narcosis, fatigue, muscle spasms, tremors, convulsions, and unconsciousness [Hathaway et al. 1991]. The onset of symptoms may be delayed for up to 2 days. Recovery from muscle spasms may occur in 24 hours, but lightheadedness and fatigue may be present for up to 3 days [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

  1. *Acute exposure:* The signs and symptoms of acute exposure to decaborane may include headache, dizziness, drowsiness, nausea, lightheadedness, fatigue, and incoordination. Based on effects seen in animals, exposure may cause redness and irritation of the eyes and eyelids, tremor, localized muscle spasm, and convulsions.

  2. *Chronic exposure:* The signs and symptoms of chronic exposure to decaborane may include headaches, fatigue, drowsiness, inability to concentrate, and lack of coordination. Based on effects seen in animals, chronic exposure may lead to jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If particulates, mists, or vapors of decaborane are inhaled, move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if decaborane or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions muse be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve decaborane and lead to worker exposures to this substance:

—Use as a reducing agent in chemical synthesis and as an olefin polymerization catalyst

—Use as a vulcanizing agent in rubber manufacture and as an anti-corrosive coating for metals

—Manufacture of high-energy fuel, rocket propellants, plastics, and polymers

—Use as a stabilizer, rayon delustrant, mothproofing agent, dye-stripping agent, fluxing agent, and oxygen scavenger

The following methods are effective in controlling worker exposures to decaborane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to decaborane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system, liver, kidneys, eyes, and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to decaborane at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system, liver, kidneys, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to decaborane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of decaborane on the central nervous system, liver, kidneys, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Borate concentrations can be measured in the serum of exposed individuals, and some sources state that serum borate concentrations greater than 20 mg/liter indicate excessive exposure. However, no biological monitoring test acceptable for routine use has yet been developed for decaborane because serum borate levels do not correlate well with airborne concentrations.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne decaborane is made using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 480 liters is collected. Analysis is conducted by inductively coupled plasma/atomic emission spectrometry. The limit of detection for this procedure is not known. Analysis is performed for total boron and then back-calculated for decaborane. This method is described in the OSHA Laboratory In-House File [OSHA 1991].

PERSONAL HYGIENE

If decaborane contacts the skin, workers should flush the affected areas immediately with 3 percent aqueous ammonia hydroxide, followed by washing with soap and water.

Clothing contaminated with decaborane should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of decaborane, particularly its potential to cause burns of the skin.

A worker who handles decaborane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, applying cosmetics, or using toilet facilities.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where decaborane or a solution containing decaborane is handled, processed, or stored.

STORAGE

Decaborane should be stored in a cool, dry, well-ventilated area in tightly sealed, weather-proof containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of decaborane should be protected from physical damage and should be stored separately from oxidizers, oxygenated solvents, dimethyl sulfoxide, heat, sparks, and open flame. Only nonsparking tools may be used to handle decaborane. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained decaborane may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving decaborane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For large liquid spills, build dikes far ahead of the spill to contain the decaborane for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility at which there are 10,000 lb or more of decaborane must comply with EPA's emergency planning requirements. (If decaborane is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 500 lb or more of decaborane are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for decaborane is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of decaborane emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although decaborane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], the EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of decaborane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent any skin contact with decaborane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to decaborane permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to decaborane.

If decaborane is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which decaborane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with decaborane. Contact lenses should not be worn if the potential exists for decaborane exposure.

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Occupational Health Guideline for Demeton

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5O)_2PSOC_2H_4SC_2H_5$
- Synonyms: Systox(R); O-O-diethyl O-(2-ethylthio)-ethyl phosphorothioate (2 parts) Demeton-O; O-O-diethyl S-(2-ethylthio)ethyl phosphorothioate (1 part) Demeton-S
- Appearance and odor: Light brown liquid with the odor of sulfur compounds

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Demeton is 0.1 milligram of Demeton per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for Demeton a Threshold Limit Value of 0.01 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Demeton can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of Demeton, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing Demeton, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to all the above symptoms, weakness, generalized twitching, and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heart beat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to Demeton may make a person more susceptible to the effects of this and related chemicals. Repeated exposures to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Demeton.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Demeton at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorder.

—Cholinesterase determination: Demeton (Systox) causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity

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in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to any new period of exposure.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed quarterly or at any time overexposure is suspected or signs or symptoms of toxicity occur.

- **Summary of toxicology**

Demeton (Systox) is an anticholinesterase agent; absorption may occur from inhalation of the vapor, by skin absorption, or by ingestion of the liquid. At least four fatal, several severe nonfatal, and a number of mild cases of Demeton intoxication have been reported. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscle, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms may occur promptly or may be delayed for up to 12 hours. After inhalation, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects, such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur, usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for weeks after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 258
2. Boiling point (2 mm Hg): 134 C (273 F)
3. Specific gravity (water = 1): 1.18
4. Vapor density (air = 1 at boiling point of Demeton): Not applicable
5. Melting point: Higher than −25 C (−13 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, phosphoric acid mist, and carbon monoxide) may be released when Demeton decomposes.
4. Special precautions: Demeton will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of Demeton.
2. Eye Irritation Level: Demeton is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of Demeton, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for Demeton is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with Demeton.
- Clothing which has had any possibility of being contaminated with Demeton should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of Demeton from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the Demeton, the person performing the operation should be informed of Demeton's hazardous properties.
- Where there is any possibility of exposure of an employee's body to Demeton, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with Demeton should be removed immediately and not reworn until the Demeton is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of Demeton contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to Demeton, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with Demeton should be immediately washed or showered with soap or mild detergent and water to remove any Demeton.
- Workers subject to skin contact with Demeton should wash any areas of the body which may have contacted Demeton at the end of each work day.
- Eating and smoking should not be permitted in areas where Demeton is handled, processed, or stored.
- Employees who handle Demeton should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Demeton may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of acaricides and insecticides	Personal protective equipment
Application as a pesticide on agricultural crops, fruits/nuts, vegetables, and ornamentals	Material substitution; personal protective equipment
Manufacture of Demeton	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If Demeton or Demeton mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If Demeton or Demeton mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If Demeton or Demeton mists penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of Demeton, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When Demeton has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If Demeton is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Demeton may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DEMETON (R)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Vapor Concentration	
1 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of Demeton; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIACETONE ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about diacetone alcohol for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{12}O_2$
- **Structure:** $(CH_3)_2C(OH)CH_2COCH_3$
- **Synonyms:** Diketone alcohol; 4-hydroxy-2-keto-4-methylpentane; 4-hydroxy-4-methyl-2-pentanone; 2-methyl-2-pentanol-4-one
- **Identifiers:** CAS 123-42-2; RTECS SA9100000; DOT 1148, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless to yellow liquid with a mild odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.62
2. Boiling point (at 760 mmHg): 169.2°C (335°F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of diacetone alcohol): 4.0
5. Melting point: -43°C (-45°F)
6. Vapor pressure: At 20°C (68°F), 0.8 mmHg; at 25°C (77°F), 1.2 mmHg
7. Miscible in water
8. Evaporation rate (butyl acetate = 1): 0.14
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.10% (1,000 ppm); at 25°C (77°F), 0.16% (1,600 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong alkalies may cause formation of flammable acetone vapors.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving diacetone alcohol.
3. Caution: Diacetone alcohol will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 57.8°C (136°F) (closed cup)
2. Autoignition temperature: 643°C (1,190°F)
3. Flammable limits in air, % by volume: Lower, 1.8; upper, 6.9
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.28 ppm
2. Eye irritation level: 100 ppm
3. Other information: Nasal irritation may occur at 100 ppm.
4. Evaluation of warning properties for respirator selection: Because of its odor, diacetone alcohol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for diacetone alcohol is 50 parts of diacetone alcohol per million parts of air (ppm) [240 milligrams of diacetone alcohol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (240 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (240 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for diacetone alcohol

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	50	240
NIOSH REL TWA	50	240
ACGIH TLV® TWA	50	240

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diacetone alcohol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: In rats and rabbits, acute oral administration or inhalation of diacetone alcohol caused narcosis, kidney damage, and liver damage (vacuolization and granulation of parenchymal cells).

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to diacetone alcohol can cause chest discomfort, narcosis, and irritation of the eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to diacetone alcohol can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to diacetone alcohol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to diacetone alcohol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or a history of chronic skin disease.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to diacetone alcohol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to diacetone alcohol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting diacetone alcohol vapors with charcoal tubes followed by desorption with 2-proponal in carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure diacetone alcohol may also be used if available. A detailed sampling and analytical method for diacetone alcohol may be found in the *NIOSH Manual of Analytical Methods* (Method number 1402).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with diacetone alcohol.

Workers should be provided with and required to use splash-proof goggles where diacetone alcohol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with diacetone alcohol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of diacetone alcohol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of diacetone alcohol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with diacetone alcohol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle diacetone alcohol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to diacetone alcohol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for diacetone alcohol

Operations	Controls
During application of nitrocellulose lacquer	Process enclosure, local exhaust ventilation, personal protective equipment
During application of paper and textile coatings, wood stains, and preservatives; during use and manufacture of artificial silk and leather, quick-drying inks, photographic film, antifreeze preparations, and hydraulic fluids	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a solvent for cellulose esters, epoxy resins, hydrocarbons, oils, fats, resin gums, dyes, tars, cements, and waxes; during use as a pigment solvent in the dyeing industry	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to diacetone alcohol, an eye-wash fountain should be provided within the immediate work area for emergency use.

If diacetone alcohol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to diacetone alcohol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If diacetone alcohol gets on the skin, wash it immediately with soap and water. If diacetone alcohol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If diacetone alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing diacetone alcohol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from diacetone alcohol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing diacetone alcohol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Diacetone alcohol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing diacetone alcohol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for diacetone alcohol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 1,250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 2,100 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 2,100 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 50 ppm (240 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIAZINON

INTRODUCTION

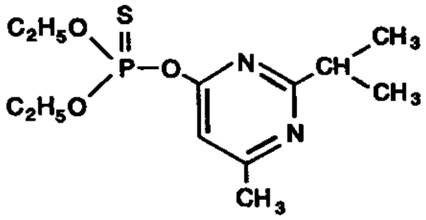
This guideline summarizes pertinent information about diazinon for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{21}N_2O_3PS$

- **Structure**



- **Synonyms**

Diazinone; isopropylmethylpyrimidyl diethyl thiophosphate; Alfa-tox; Basudin; Flytrol; Garden Tox; Knox-out; Nipsan; Oleod-iazinon; O,O-diethyl O-(2-isopropyl-4-methyl-6-pyrimidyl)thionophosphate.

- **Identifiers**

1. CAS No.: 333-41-5
2. RTECS No.: TF3325000
3. DOT NA: 2783 55
4. DOT label: None

- **Appearance and odor**

Pure diazinon is a colorless liquid; however, the technical grade of diazinon has a faint odor and is pale yellow to dark brown in color. Diazinon is an organophosphate pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 304.4
2. Boiling point (0.002 mm Hg): 83° to 84°C (181° to 183°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.00041 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; soluble in organic solvents; miscible with petroleum ether, alcohol, cyclohexane, ether, and benzenes.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Water, heat, sparks, and open flame.

2. Incompatibilities: Contact of diazinon with water, copper-containing compounds, oxidizers, acids, or bases may cause a violent reaction.

3. Hazardous decomposition products: Toxic particulates and gases (such as oxides of nitrogen, phosphorus, sulfur, and carbon monoxide) may be released in a fire involving diazinon.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to diazinon.

1. Flash point: 180°F (82.2°C)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving diazinon should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of diazinon may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diazinon. Chemical protective clothing specifically recommended for diazinon may not provide thermal protection unless so stated by the manufacturer. Structural firefighters' protective clothing may not provide protection against permeation by diazinon.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diazinon [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has eatablished a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diazinon a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH also assigns a "Skin" notation to diazinon [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation and cholinesterase inhibition associated with diazinon exposure. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to diazinon.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diazinon can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Diazinon is classified as a moderately toxic organophosphate pesticide [EPA 1989]; it is a cholinesterase inhibitor in experimental animals. Applied to the skin of rabbits under open conditions, 500 mg of diazinon caused moderate systemic toxicity but no primary irritation [NIOSH 1993]. The dermal LD$_{50}$ in rabbits is 180 mg/kg

[NIOSH 1993]. The oral LD_{50} in rats is 66 mg/kg, and the LC_{50} in the same species is 3500 mg/m^3 for 4 hours [NIOSH 1993]. In one study, rats fed diazinon at a dose of 50 mg/kg/day for 72 weeks showed complete inhibition of red blood cell cholinesterase activity and marked inhibition of brain cholinesterase activity but no other signs of toxicity [ACGIH 1991]. In another study, rats fed 10, 100, or 1,000 ppm diazinon in the diet for 72 weeks showed no adverse effects [Clayton and Clayton 1981]. Dogs fed diazinon at a dose of 9.3 mg/kg/day promptly lost weight and showed signs of poisoning and developed tremor; at a dose of 4.6 mg/kg/day for 12 weeks, reversible cholinesterase activity was seen in these animals [Hayes 1982]. Rhesus monkeys tolerated diazinon in the diet at a dose of 0.05 mg/kg/day for 2 years without effect; inhibition of both plasma and red blood cell cholinesterase was moderate or erratic when the dose was increased to 0.5 mg/kg/day, and marked decreases in cholinesterase activity occurred at 5 mg/kg/day [Hayes 1982].

2. *Effects on Humans:* Diazinon is an organophosphate pesticide of moderate toxicity [EPA 1989]; it is a cholinesterase inhibitor in humans. In contact with the skin, diazinon may cause allergic skin reactions; this substance has also caused fatalities when absorbed through the skin [NLM 1992]. In a series of tests involving 2 to 4 volunteers, oral diazinon doses of 0.05 mg/kg/day for 28 days caused a 35- to 40-percent reduction in cholinesterase activity in plasma but had no effect on red blood cell cholinesterase activity [ACGIH 1991]. Diazinon administered at an oral dose of 0.02 mg/kg/day for 37 days caused a 14-percent reduction in plasma cholinesterase activity, an amount difficult to distinguish from normal variation [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to diazinon may cause cholinesterase inhibition. The signs and symptoms of cholinesterase inhibition include headache, dizziness, anxiety, restlessness, confusion, bizarre behavior, muscle twitching, weakness, tremor, incoordination, nausea, vomiting, diarrhea, abdominal cramps, sweating, salivation, tearing, blurred vision, constricted pupils, chest tightness, wheezing, cough, rales, bradycardia or tachycardia, and hypertension.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to low doses of cholinesterase inhibitors include, in addition to those listed above, anorexia, weakness, and malaise.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of diazinon. diazinon can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of diazinon are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diazinon or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diazinon and may result in worker exposures to this substance:

—Use as a soil insecticide and lawn and garden spray

—Use for insect control on fruits, vegetables, tobacco, forage, field crops, and ornamentals

—Manufacture and formulation of diazinon-containing pesticides

—Use as a pet spray

The following methods are effective in controlling worker exposures to diazinon, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to diazinon, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the cholinesterase activity level of the blood (plasma and red blood cells).

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diazinon at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reductions in plasma or red blood cell cholinesterase activity. To establish a baseline, plasma and red blood cell cholinesterase activity readings should be taken before the worker is exposed to organophosphate pesticides.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diazinon on plasma or red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of plasma or red blood cell cholinesterase activity is a nonspecific, qualitative indicator of exposure to organophosphorus chemicals such as diazinon. Red blood cell cholinesterase activity can be an indicator either of acute overexposure or of cumulative chronic exposure to diazinon. A red blood cell cholinesterase level that is equal to 70 percent of the worker's preexposure baseline level is recommended by some sources as a biological exposure index for organophosphates.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne diazinon is determined using an OSHA Versatile Sampler (OVS-2), 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh), with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.09 and is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Diazinon can be absorbed through the skin in toxic amounts. Therefore, if diazinon contacts the skin, workers should repeatedly and vigorously wash the affected areas immediately with soap and water.

Clothing contaminated with diazinon should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles diazinon should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diazinon or a solution containing diazinon is handled, processed, or stored.

STORAGE

Diazinon should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diazinon should be protected from physical damage and should be stored separately from water, oxidizers, acids or bases, heat, sparks, and open flame. Because containers that formerly contained diazinon may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diazinon, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Water spray may be used to reduce vapors.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the diazinon for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diazinon is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for diazinon is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hour period, in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diazinon emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diazinon is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 *et seq.*], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diazinon exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with diazinon. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to diazinon permeation. However, permeation tests with similar compounds (other organophosphorus compounds) have shown that a laminate of Viton/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diazinon. If diazinon is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diazinon might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diazinon.

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Occupational Health Guideline for Diazomethane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2N_2
- Synonyms: Azimethylene; diazirine
- Appearance: Yellow gas. When stored under pressure, diazomethane can be in the liquid form.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diazomethane is 0.2 part of diazomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of diazomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diazomethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to diazomethane vapor may cause severe irritation of the eyes, nose, throat, skin, and lungs. Symptoms include headache, weakness, cough, fever, chest pains, shortness of breath, and wheezing. The onset of symptoms after exposure may be delayed. Skin and mucous membrane exposure to liquids containing diazomethane may cause burns with the loss of the skin or mucous membrane. If any of these symptoms appear, get medical attention immediately.

2. Long-term Exposure: Prolonged or repeated exposure to diazomethane may lead to sensitization. Should sensitization occur, a person may experience asthma-like symptoms or fever from exposure to concentrations of diazomethane which had previously caused no symptoms. Diazomethane has been reported to cause cancer of the lungs in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diazomethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diazomethane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of respiratory system should be stressed.

—14" x 17" chest roentgenogram: Diazomethane may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Diazomethane is reported to cause temporary pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Diazomethane gas is a severe respiratory irritant and sensitizer. It is one of the most dangerous products of the chemical laboratory, causing irritation of the eyes, chest pain, cough, fever, and severe asthmatic attacks. Exposure of cats to 175 ppm for 10 minutes resulted in pulmonary edema and hemorrhage, with death occurring in 3 days. A chemist briefly exposed to an unknown concentration in a laboratory developed a violent cough and shortness of breath leading to severe pul-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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monary edema; symptoms completely subsided within 2 weeks. In a fatal incident, another chemist exposed to an unknown concentration of diazomethane, as well as other irritant gases, experienced immediate respiratory distress leading to pneumonitis and death on the fourth day after exposure. A physician exposed to diazomethane from a laboratory spill noted only a faint odor, but immediately experienced severe headache, cough, mild anterior chest pain, generalized aching of muscles, and a sensation of overwhelming tiredness. Within 5 minutes he was stuporous, and on early admission to hospital was markedly flushed and feverish; he recovered in approximately 48 hours. Subsequent exposure to trace amounts of the gas produced wheezing, cough, and malaise, leading to the suspicion that this substance may have a sensitizing, as well as an irritating, effect upon the respiratory system. Skin irritation and sensitization occurs. Also mutagenic and carcinogenic effects have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 42
2. Boiling point (760 mm Hg): −23 C (−9 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of diazomethane): 1.4
5. Melting point: −145 C (-229 F)
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not pertinent

- **Reactivity**

1. Conditions contributing to instability: Diazomethane may explode when not diluted with other inert gases such as nitrogen. Exposure of diazomethane gas or solutions in solvents to sunlight or other bright illumination may cause explosions. Contact with rough edges such as ground glass may cause explosions.
2. Incompatibilities: Contact of diazomethane gas with alkali metals or drying agents such as calcium sulfate will cause explosions.
3. Hazardous decomposition products: Data not available
4. Special precautions: Barriers or shields should be utilized to protect employees from accidental explosions.

- **Flammability**

1. Flash point: Not pertinent
2. Autoignition temperature: Pure material explodes above 150 C (302 F). Impure material explodes at lower temperature.
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: Patty reports that diazomethane has a musty odor. No quantitative data are available, however, relating the odor to air concentrations.
2. Eye Irritation Level: Grant reports that "irritation of the eye from exposure to the gas has developed occasionally among those working with this substance." The concentrations causing eye irritation are not given.
3. Other Information: Patty reports that diazomethane is a severe respiratory tract irritant, but the concentrations producing this irritation are not given.
4. Evaluation of Warning Properties: Patty reports that "the warning properties of diazomethane are not adequate to prevent serious intoxication or fatalities." Based upon this report and upon the lack of quantitative data relating warning properties to air concentrations of diazomethane, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube containing XAD-2 resin coated with octanoic acid, followed by desorption with carbon disulfide and gas chromatographic analysis. An analytical method for diazomethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming contaminated with liquid diazomethane or solutions containing diazomethane or from becoming frozen from contact with vessels containing liquid diazomethane.
- Clothing wet with flammable solutions containing diazomethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diazomethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diazomethane, the person performing the operation should be informed of diazomethane's hazardous properties.
- Any clothing which becomes wet with liquid diazomethane or flammable solutions containing diazomethane should be removed immediately and not reworn until the flammable liquids are removed from the clothing.
- Non-impervious clothing which becomes contaminated with solutions containing diazomethane should be removed promptly and not reworn until the diazomethane is removed from the clothing.
- Employees should be provided with and required to use safety goggles where there is any possibility of liquid diazomethane or solutions containing diazomethane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid diazomethane or solutions containing diazomethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with solutions containing diazomethane should be promptly washed or showered with soap or mild detergent and water to remove any solutions.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diazomethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as methylating agent in chemical analysis and laboratory organic synthesis	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid diazomethane or solutions containing diazomethane get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid diazomethane or solutions containing diazomethane get on the skin, immediately flush the contaminated skin with water. If liquid diazomethane or solutions containing diazomethane soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of diazomethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If diazomethane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If diazomethane is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

- Waste disposal method:

Diazomethane may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974.

RESPIRATORY PROTECTION FOR DIAZOMETHANE

Condition	**Minimum Respiratory Protection* Required Above 0.2 ppm**
Gas Concentration	
2 ppm or less**	Any supplied-air respirator. Any self-contained breathing apparatus.
10 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Diborane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: B_2H_6
- Synonyms: Boroethane
- Appearance and odor: Colorless gas with a repulsive, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diborane is 0.1 part of diborane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.1 milligram of diborane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diborane can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Diborane may cause tightness in the chest, cough, inability to take a deep breath, and chest pain. Severe breathing difficulties may occur. These difficulties may be delayed in onset. High concentrations of diborane may irritate the eyes.

2. Long-term Exposure: Prolonged exposure to low concentrations of diborane may cause headache, lightheadedness, fatigue, muscular weakness, and tremors. It has caused liver and kidney damage in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diborane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diborane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs, nervous system, liver, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Diborane causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Diborane is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Diborane gas is a pulmonary irritant. The LC50 for rats was 50 ppm for 4 hours; in other animal experiments, acute exposure caused pulmonary edema and hemorrhage and temporary damage to the liver and kidneys. In humans, overexposure results in a sensation of tightness in the chest leading to precordial pain, shortness of breath, nonproductive cough, and sometimes nausea. Prolonged exposure to low concentrations causes headache, light-headedness, vertigo, chills and, less frequently, fever; fatigue or weakness occurs and may persist for several hours; tremor or muscular fasciculations occur infrequently and are usually localized and of short duration. Diborane gas has not been found to have significant effects upon contact with skin or mucous

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membranes, although high concentrations may cause eye irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 27.7
2. Boiling point (760 mm Hg): −92 C (−134 F)
3. Specific gravity (water = 1): 0.47 (liquid)
4. Vapor density (air = 1 at boiling point of diborane): 0.96
5. Melting point: −165 C (−265 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts rapidly to form hydrogen gas
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above −18 C (0 F). Containers are usually stored in "dry ice." Ignites spontaneously in moist air at room temperature.
2. Incompatibilities: Contact with air or halogenated compounds will cause fires and explosions. Contact with aluminum, lithium, and other active metals forms hydrides which may ignite spontaneously. Diborane reacts with many oxidized surfaces as a strong reducing agent.
3. Hazardous decomposition products: Toxic gases and vapors (such as boron oxide smoke) may be released in a fire involving diborane.
4. Special precautions: Diborane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: 38 − 52 C (100 − 125 F)
3. Flammable limits in air, % by volume: Lower: 0.8; Upper: 98
4. Extinguishant: Stop flow of gas, or let fire burn.

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, the nauseating odor of diborane is "not a reliable warning of toxic exposure." No quantitative information is available concerning the threshold of odor, however.
2. Eye Irritation Level: Diborane is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of diborane, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for diborane had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diborane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a reducing agent in the synthesis of organic chemical intermediates; use as a component or additive for high-energy fuels; use as a catalyst in olefin polymerization	Process enclosure; personal protective equipment
Use in electronics industry to improve crystal growth or to impart electrical properties in pure crystals	Process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If strong concentrations of diborane gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Breathing**

If a person breathes in large amounts of diborane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If diborane is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR DIBORANE

Condition	**Minimum Respiratory Protection* Required Above 0.1 ppm**
Gas Concentration	
1 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against diborane. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIBROMOCHLOROPROPANE

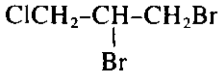
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about dibromochloropropane (DBCP) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_3H_5Br_2Cl$
- **Structure:**



$\mathrm{ClCH_2{-}\underset{\underset{\displaystyle Br}{|}}{CH}{-}CH_2Br}$

- **Synonyms:** 1-Chloro-2,3-dibromopropane; DBCP; 1,2-dibromo-3-chloropropane
- **Identifiers:** CAS 96-12-8; RTECS TX8750000; DOT 2872, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Dense yellow or amber liquid or granular solid with a pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 236.35
2. Boiling point (at 760 mmHg): 195 °C (383 °F)
3. Specific gravity (water = 1): 2.093
4. Melting point: 6 °C (43 °F)
5. Vapor pressure at 20 °C (68 °F): 0.8 mmHg
6. Solubility in water, g/100 g water at 20 °C (68 °F): 0.1
7. Saturation concentration in air (approximate) at 20 °C (68 °F): 0.1% (1000 ppm)

- **Reactivity**

1. Incompatibilities: DBCP reacts with chemically active metals such as aluminum, magnesium, and tin alloys.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen bromide, hydrogen chloride, and carbon monoxide) may be released in a fire involving DBCP.
3. Caution: DBCP will attack some rubber materials and coatings.

- **Flammability**

1. Flash point: 77 °C (170 °F) (open cup)
2. Extinguishant: Carbon dioxide or dry chemical
3. Class IIIA Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

1. Odor threshold: 0.01-0.03 ppm
2. Evaluation of warning properties for respirator selection: Because of the lack of odor at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), DBCP is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) considers DBCP to be a cancer hazard. The current OSHA permissible exposure limit (PEL) for DBCP is 1 part of DBCP per billion parts of air (ppb) as a time-weighted average (TWA) concentration over an 8-hour workshift; the employer shall assure that no employee is exposed to eye or skin contact with DBCP. The NIOSH REL is 10 ppb as a TWA [0.1 milligrams of DBCP per cubic meter of air (mg/m^3)] for up to a 10-hour workshift, 40-hour workweek; however, the NIOSH REL has been superseded by the OSHA standard promulgated in 1978. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have an assigned threshold limit value (TLV®) for DBCP.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

DBCP may cause adverse health effects following exposure via inhalation or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats, acute inhalation or oral administration of DBCP caused central nervous system depression with sluggishness and loss of muscular coordination (ataxia), weight loss, and decreased spermatogenesis; acute dermal exposure caused dermal and subcutaneous tissue destruction (necrosis).

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Subchronic inhalation of DBCP by rats, guinea pigs, rabbits, or monkeys produced necrosis of the liver, kidney, spleen, testes, or seminiferous tubules; reduction in sperm count; abnormal sperm; or inhibition of the estrous cycle. Cancers of the nasal cavity, tongue, pharynx, lungs, stomach, adrenal glands, or mammary glands have been reported for rats or mice chronically exposed to DBCP by inhalation or oral administration.

2. *Effects on humans:* Low-level repeated or prolonged exposure of male workers has been associated with low sperm count, chromosome abnormality, sterility, decreased testicular size, and increased level of follicle stimulating hormone. These effects have not been associated with exposure in previous years, indicating that they may be reversible following removal from exposure.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to DBCP can cause drowsiness, nausea, vomiting, and irritation of the eyes, nose, throat and skin.

2. *Long-term (chronic):* Exposure to DBCP can cause congestion or fluid in the lungs and inflammation of the eyes or skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to DBCP, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, urinary tract, and reproductive and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DBCP at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DBCP. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function and integrity of the eyes, skin, liver, kidneys, urinary tract, and respiratory and reproductive systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DBCP may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset or reproductive SHE's include: Infertility in exposed males.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to DBCP should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

There are no NIOSH validated sampling and analytical methods for DBCP.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with DBCP.

Workers should be provided with and required to use dust- and splash-proof safety goggles where DBCP or other dust may come in contact with the eyes.

SANITATION

Clothing which is contaminated with DBCP should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DBCP from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DBCP's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with DBCP should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DBCP should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DBCP may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for dibromochloropropane

Operations	Controls
During the manufacture of DBCP	Completely enclosed processes, local exhaust ventilation, personal protective equipment
During the formulation of DBCP into pesticides and fumigants	Local exhaust ventilation, protective clothing and equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DBCP, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DBCP gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to DBCP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DBCP gets on the skin, wash it immediately with soap and water. If DBCP penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DBCP is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing DBCP, absorb on paper towels and place in an appropriate container. Place towels

in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from DBCP vapors. Burn the paper in a suitable location away from combustible materials.

4. Large quantities of liquids containing DBCP may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. DBCP should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

5. DBCP liquid or solid may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 2.—Respiratory protection for dibromochloropropane

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-n-DIBUTYLAMINOETHANOL

INTRODUCTION

This guideline summarizes pertinent information about 2-n-dibutylaminoethanol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{23}NO$

- **Structure**

$(C_4H_9)_2NCH_2CH_2OH$

- **Synonyms**

2-Dibutylaminoethanol; N,N-di-n-butylaminoethanol; beta-n-dibutylaminoethyl alcohol; N,N-dibutylethanolamine; N-N-dibutyl-n-(2-hydroxyethyl)amine; DBAE

- **Identifiers**

1. CAS No.: 102-81-8
2. RTECS No.: KK3850000
3. DOT UN: 2873 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

2-n-Dibutylaminoethanol is a combustible, colorless liquid with a faint, amine-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 173.3
2. Boiling point (760 mm Hg): 224° to 232°C (435° to 450°F)
3. Specific gravity (water = 1): 0.86 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of 2-n-dibutylaminoethanol): 6.0
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.1 mm Hg
7. Solubility: Slightly soluble in water; soluble in methanol, ethyl ether, acetone, gasoline, benzene, and ethyl acetate.

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Contact of 2-n-dibutylaminoethanol with oxidizing materials causes a violent reaction.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and oxides of nitrogen) may be released in a fire involving 2-n-dibutylaminoethanol.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to 2-n-dibutylaminoethanol.

1. Flash point: 93°C (200°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, water spray, or foam to fight fires involving 2-n-dibutylaminoethanol.

Fires involving 2-n-dibutylaminoethanol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of 2-n-dibutylaminoethanol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2-n-dibutylaminoethanol. Chemical protective clothing that is specifically recommended for 2-n-dibutylaminoethanol may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving 2-n-dibutylaminoethanol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 2-n-dibutylaminoethanol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (14 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-n-dibutylaminoethanol a threshold limit value (TLV) of 2 ppm (14 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 2-n-dibutylaminoethanol [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on acetylcholinesterase inhibition in vitro and weight loss in animals associated with 2-n-dibutylaminoethanol [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-n-dibutylaminoethanol can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* 2-n-Dibutylaminoethanol causes irritation of the eyes and skin on acute exposure and liver and kidney damage on longer exposure. In contact with the skin of rabbits, 2-n-dibutylaminoethanol caused severe irritation [NIOSH 1993]. Application of 0.005 ml undiluted 2-n-dibutylaminoethanol to the

eyes of rabbits caused severe corneal injury [Grant 1986]. The oral LD_{50} in rats is 1,070 mg/kg, and the dermal LD_{50} in rabbits is 1,680 mg/kg [NIOSH 1993]. One of 5 rats exposed to a 70-ppm concentration of 2-n-dibutylaminoethanol for 6 hours/day, 5 days/week for 1 week died; in addition, compared with controls, exposed rats had a 57-percent average body weight loss, a 2-fold increase in liver- and kidney-to-body weight ratios, a 10-fold increase in serum bilirubin, a slightly elevated clotting time, and an elevated hematocrit. Exposure to a 22-ppm concentration of 2-n-dibutylaminoethanol on the same regimen for 27 weeks produced no changes in exposed rats [ACGIH 1991]. Rats fed 2-n-dibutylaminoethanol for 5 weeks at doses greater than 0.13 g/kg/day had elevated kidney-to-body weight ratios at autopsy, although no histologic changes were evident [ACGIH 1991].

2. *Effects on Humans:* Exposure to 2-n-dibutylaminoethanol causes irritation of the eyes, nose, throat, and skin in humans [NJDH 1987]. By analogy with the effects caused by chemically similar compounds, exposure to 2-n-dibutylaminoethanol may also cause allergic reactions, such as asthma or skin rashes [NJDH 1987]. In vitro studies show that 2-n-dibutylaminoethanol inhibits the enzyme acetylcholinesterase [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 2-n-dibutylaminoethanol include redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, redness and inflammation of the skin, and acetylcholinesterase inhibition. Symptoms of acetylcholinesterase inhibition include headache, sweating, nausea, vomiting, diarrhea, muscle twitching, coma, and death.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to 2-n-dibutylaminoethanol may include abdominal tenderness, enlarged liver, jaundice, and pus or blood in the urine.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2-n-dibutylaminoethanol. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2-n-dibutylaminoethanol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve 2-n-dibutylaminoethanol and lead to worker exposure to this substance:

—Organic synthesis

The following methods are effective in controlling worker exposures to 2-n-dibutylaminoethanol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to 2-n-dibutylaminoethanol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, respiratory system, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-n-dibutylaminoethanol at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with allergies or with diseases of the liver, kidneys, respiratory system, or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-n-dibutylaminoethanol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-n-dibutylaminoethanol on the liver, kidneys, respiratory system, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-n-dibutylaminoethanol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 2-n-dibutylaminoethanol is made using a silica gel tube (300/150 mg sections, 45/60 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 24 liters is collected. Immediately after sampling, each section of the tube should be transferred to a separate vial containing 2 milliliters of desorbing solution (0.12 M HCl in 4:1 methanol:water). Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1992] and in Method No. 2007 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If 2-n-dibutylaminoethanol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with 2-n-dibutylaminoethanol should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the irritant properties of 2-n-dibutylaminoethanol.

A worker who handles 2-n-dibutylaminoethanol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2-n-dibutylaminoethanol is handled, processed, or stored.

STORAGE

2-n-Dibutylaminoethanol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of 2-n-dibutylaminoethanol should be protected from physical damage and should be stored separately from oxidizers (such as perchlorates, peroxides, and permanganates), heat, sparks, and open flame. To prevent static sparks, all equipment used in the manufacturing, use, or storage of this substance should be grounded and bonded. Because containers that formerly contained 2-n-dibutylaminoethanol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-n-dibutylaminoethanol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use water spray to reduce vapors.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the 2-n-dibutylaminoethanol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  2-n-Dibutylaminoethanol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-n-dibutylaminoethanol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 2-n-dibutylaminoethanol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although 2-n-dibutylaminoethanol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-n-dibutylaminoethanol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as necessary) should be worn to prevent prolonged or repeated skin contact with 2-n-dibutylaminoethanol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-n-dibutylaminoethanol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-n-dibutylaminoethanol.

If 2-n-dibutylaminoethanol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-n-dibutylaminoethanol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-n-dibutylaminoethanol. Contact lenses should not be worn when working around this material.

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Occupational Health Guideline for Dibutyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_4H_9O)_2(OH)PO$
- Synonyms: Dibutyl acid o-phosphate; di-n-butyl hydrogen phosphate; dibutyl phosphoric acid
- Appearance and odor: Colorless to brown odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dibutyl phosphate is 1 part of dibutyl phosphate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of dibutyl phosphate per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dibutyl phosphate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Dibutyl phosphate may cause irritation of the eyes, nose, throat, and lungs. It may also cause headaches.

2. Long-term Exposure: Repeated or prolonged exposure to dibutyl phosphate may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dibutyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dibutyl phosphate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from dibutyl phosphate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of dibutyl phosphate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Dibutyl phosphate can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Dibutyl phosphate vapor is a respiratory irritant. In rats the oral LD50 is 3.2 g/kg. Data on effects in humans are sparse; workers exposed to unspecified concentrations of vapor complained of respiratory irritation and headache. It is a moderately strong acid and could be expected to be irritating on contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 210
2. Boiling point (760 mm Hg): Higher than 100 C (212 F) (decomposes)
3. Specific gravity (water = 1): 1.06
4. Vapor density (air = 1 at boiling point of dibutyl phosphate): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F):

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving dibutyl phosphate.

4. Special precautions: Liquid dibutyl phosphate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dibutyl phosphate.

2. Eye Irritation Level: Dibutyl phosphate vapor is not known to be an eye irritant.

3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of dibutyl phosphate, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for dibutyl phosphate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid dibutyl phosphate, where skin contact may occur.
- Clothing wet with liquid dibutyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dibutyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dibutyl phosphate, the person performing the operation should be informed of dibutyl phosphate's hazardous properties.
- Where exposure of an employee's body to liquid dibutyl phosphate may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with dibutyl phosphate should be removed promptly and not reworn until the dibutyl phosphate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dibutyl phosphate may contact the eyes.

SANITATION

- Skin that becomes contaminated with dibutyl phosphate should be promptly washed or showered with soap or mild detergent and water to remove any dibutyl phosphate.
- Employees who handle liquid dibutyl phosphate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dibutyl phosphate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a catalyst in manufacture of phenolic and urea resins	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in metal separation and extraction	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid dibutyl phosphate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dibutyl phosphate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid dibutyl phosphate soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of dibutyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid dibutyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid dibutyl phosphate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Dibutyl phosphate may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Dibutyl Phosphate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
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RESPIRATORY PROTECTION FOR DIBUTYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
10 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
125 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 125 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dibutylphthalate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_4(CO_2C_4H_9)_2$
- Synonyms: DBP; dibutyl 1,2-benzenedicarboxylate
- Appearance and odor: Colorless, oily liquid with a very weak, aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dibutylphthalate is 5 milligrams of dibutylphthalate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dibutylphthalate can affect the body if it is swallowed, comes in contact with the eyes or skin, or is inhaled as a mist or spray.

- **Effects of overexposure**

Swallowing dibutylphthalate may cause nausea, dizziness, light sensitivity, and watering and redness of the eyes. Overexposure to hot vapors or mists of dibutylphthalate may cause nose and throat irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dibutylphthalate.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to dibutylphthalate at potentially hazardous levels.

- **Summary of toxicology**

Extensive experience with dibutylphthalate as an insect repellant has shown that it is relatively non-irritating to the skin, eyes, and mucous membranes. Aerosols from heated dibutylphthalate may cause irritation of the eyes and upper respiratory tract. In one report of a human case, accidental ingestion of ten grams of this compound by a chemical operator produced nausea and dizziness with lacrimation, photophobia, and conjunctivitis, but recovery was prompt and uneventful. Animal experiments to determine dermal and oral toxicity of dibutylphthalate showed that extremely high doses were considered necessary to produce toxic effects. Dibutylphthalate was found to be teratogenic by intraperitoneal injection of doses representing $\frac{1}{10}$, $\frac{1}{5}$, and $\frac{1}{3}$ of the LD50 value into female rats at the 5th, 10th, and 15th day of gestation. This probably is of no significance in industrial exposures.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 278
  2. Boiling point (760 mm Hg): 335 C (635 F)
  3. Specific gravity (water = 1): 1.05
  4. Vapor density (air = 1 at boiling point of dibutylphthalate): 9.6
  5. Melting point: −37 C (−35 F)
  6. Vapor pressure at 20 C (68 F): Less than 0.01 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.45
  8. Evaporation rate (butyl acetate = 1): Almost zero
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dibutylphthalate.

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4. Special precautions: None

- **Flammability**

1. Flash point: 157 C (315 F) (closed cup)
2. Autoignition temperature: 403 C (757 F)
3. Flammable limits in air, % by volume: Lower: 0.5 (calculated at flash point)
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

According to Grant, "contact with the surface of human eyes has occurred by accidental droplet splash as well as by experimental application, and this has caused immediate, severe, stinging pain. The pain stimulated profuse tearing, which washed the oily liquid away, and the eyes were not appreciably damaged."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dibutylphthalate on a filter, followed by extraction with carbon disulfide, and gas chromatographic analysis. An analytical method for dibutylphthalate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use splash-proof safety goggles where liquid dibutylphthalate may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dibutylphthalate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of polyvinyl acetate surface coatings by spraying, dipping, or crushing	Local exhaust ventilation; personal protective equipment
Liberation during spray application of polyester and epoxy resins	Local exhaust ventilation; personal protective equipment
Liberation during hand and dip applications of polyvinyl acetate, and polyester and epoxy resins	General dilution ventilation
Liberation during molding and forming of cellulose acetate butyrate, acetate, propionate, and polyvinyl acetate	Local exhaust ventilation; personal protective equipment
Liberation during application of polyvinyl acetate adhesives, both solvent and hot-melt types	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of nitrile rubber; during molding of polyester and epoxy articles	General dilution ventilation
Liberation during manufacture of polyvinyl acetate surface coatings	General dilution ventilation
Use during spray application of nitrocellulose lacquer surface coatings, including paper coatings	Local exhaust ventilation

Operation	Controls
Liberation during forming of ethyl cellulose articles; during production of polyvinyl acetate; during production of cellulose acetate butyrate, cellulose acetate propionate, and polyvinyl acetate adhesives	General dilution ventilation
Liberation during brush application of nitrocellulose surface coatings; during manufacture of polyester and epoxy resins; during manufacture of nitrocellulose surface coatings	General dilution ventilation
Liberation during manufacture of explosives and propellants	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dibutylphthalate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention if any discomfort continues. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dibutylphthalate saturates the clothing, remove and clean the clothing before wearing it again. Wash any dibutylphthalate from the skin regularly, particularly when there has been much skin contact. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of dibutylphthalate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dibutylphthalate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing respiratory protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dibutylphthalate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

- Waste disposal methods:

Dibutylphthalate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Dibutylphthalate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Singh, A. R., et al.: "Teratogenicity of Phthalate Esters in Rats," *Journal of Pharmaceutical Sciences,* 61:51-55, 1972.
- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Dibutylphthalate*, New York, 1971.

RESPIRATORY PROTECTION FOR DIBUTYLPHTHALATE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
250 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
9300 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 9300 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICHLOROACETYLENE

INTRODUCTION

This guideline summarizes pertinent information about dichloroacetylene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_2Cl_2

- **Structure**

  $ClC \equiv CCl$

- **Synonyms**

  Dichloroethyne; 1,2-dichloroacetylene

- **Identifiers**

  1. CAS No.: 7572-29-4
  2. RTECS No.: AP1080000
  3. DOT UN: May not be transported.
  4. DOT label: Forbidden

- **Appearance and odor**

  Dichloroacetylene is a combustible, volatile, self-reactive liquid with an isocyanide-like odor. This material is not produced or used commercially; it is an undesirable byproduct of the dehydrochlorination or incomplete incineration of trichloroethylene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 94.9
  2. Boiling point (760 mm Hg): Explodes on boiling at 32° to 33°C (90° to 91°F)
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: -66° to -64.2°C (-86.8° to -83.6°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; soluble in alcohol, ethanol, and acetone
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: shock, heat, sparks, open flame, acids, oxidizing materials, or contact with the air.

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2. Incompatibilities: Contact of dichloroacetylene with air causes autoxidation and may cause an explosion; contact with acids or oxidizing materials also may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide, phosgene, and chlorine) may be released in a fire involving dichloroacetylene.

4. Special precautions: Dichloroacetylene explodes or ignites on contact with air and explodes if it reaches boiling temperature. Also, in air, unstabilized dichloroacetylene decomposes to phosgene, chloroform, carbon tetrachloride, trichloroacryloyl chloride, and hexachlorobutadiene.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to dichloroacetylene. However, this substance is known to be spontaneously combustible and to pose a severe explosion hazard when exposed to heat or shock.

1. Flash point: Spontaneously combustible

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use carbon dioxide, water spray, or regular foam. Do not use any chemical extinguishants because dichloroacetylene is shock-sensitive and contact with the surface of dry chemicals may increase its explosive potential. Do not use more water than is necessary to extinguish the fire because it will scatter the fire.

Fires involving dichloroacetylene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dichloroacetylene because poisonous gases (such as phosgene and hydrogen chloride) may be produced in a fire.

XPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dichloroacetylene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.4 mg/m^3) as a ceiling limit. A worker's exposure to dichloroacetylene shall at no time exceed this ceiling level [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dichloroacetylene a ceiling limit value of 0.1 ppm (0.9 mg/m^3), which should not be exceeded during any part of the working day [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer, neurotoxicity, and CNS depression and also the formation of kidney tumors in animals associated with dichloroacetylene exposure. The ACGIH limit is based on the risk of nausea and other systemic effects associated with exposure to dichloroacetylene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dichloroacetylene can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dichloroacetylene causes kidney and liver damage and cancer in experimental animals. In mice, a 1-hr LC_{50} of 124 ppm and a 4-hr LC_{50} of 19 ppm have been reported. The cause of death was kidney injury [Clayton and Clayton 1981]. A 6-hr LC_{50} in mice of 19 ppm has also been reported [RTECS 1991]. Exposure to dichloroacetylene concentrations of 126, 202, or 307 ppm for 1 hour or to 17 to 23 ppm for 6 hours caused neuropathological changes, kidney and liver damage, and death among rabbits [Clayton and Clayton 1981; IARC 1986]. Rats exposed continuously to a 2.8-ppm concentration of dichloroacetylene for 90 days became emaciated and showed hind limb weakness and kidney injury, and one animal became blind [Grant 1986]. Rats exposed for 6 hours/day, 5 days/week for 6

weeks to a 9.8-ppm concentration of dichloroacetylene (along with 50-ppm trichloroacetylene) or to 15.5 ppm dichloroacetylene (along with 150 ppm trichloroacetylene) were unkempt in appearance and showed signs of respiratory distress; rats in the 15.5-ppm group also showed marked kidney injury at autopsy [Clayton and Clayton 1981]. Dichloroacetylene has been tested for carcinogenicity in inhalation bioassays in mice and rats. Male mice showed dose-related increases in the incidence of adenocarcinomas of the kidney, and rats of both sexes showed an increased incidence of lymphomas and also developed benign tumors of the liver and kidney [IARC 1986]. Based on these data, the International Agency for Research on Cancer has concluded that there is limited evidence that dichloroacetylene is carcinogenic in animals [IARC 1986].

2. *Effects on Humans:* In humans, dichloroacetylene causes eye irritation, headache, nausea, and vomiting as well as nervous system injury and death. As a neurotoxin, dichloroacetylene has an affinity for the cranial nerves [IARC 1986]. Exposure to a 0.5- to 1-ppm concentration of dichloroacetylene for prolonged (not further specified) periods caused nausea in 85 percent of exposed individuals [ACGIH 1991]. Members of a submarine crew developed loss of appetite, nausea that progressed to vomiting, itching around the eyes, headache, sore gums, intense pain in the upper jaw, and facial and oral herpes 3 to 4 days after exposure to dichloroacetylene [IARC 1986]. Tank car cleaners developed fatigue, headache, nausea, and vomiting; these workers also experienced a loss of sensation in the trigeminal nerve distribution that persisted for periods ranging from several days to years [IARC 1986]. Thirteen cases of dichloroacetylene-induced cranial nerve palsy and nine cases of herpes were reported in the 1940s. One patient died 3 days after exposure and a second died 13 days later; autopsy revealed cerebral edema in both of these cases [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dichloroacetylene include redness, inflammation, and itching of the eyes and eyelids, weakness of the eye muscles, headache, nausea, vomiting, sore gums, painful jaws, loss of sensation in the lips and mucous membranes, fatigue, and facial and oral herpes characterized by painful blisters around the mouth.

2. *Chronic exposure:* Based on effects seen in animals, chronic exposure to dichloroacetylene may cause liver or kidney damage, with jaundice, enlarged and tender liver, and pus, protein, or blood in the urine.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dichloroacetylene. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dichloroacetylene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may evolve dichloroacetylene and lead to worker exposures to this substance:

—Thermal dehydrochlorination of trichloroethylene

—Degradation of trichloroethylene, vinylidene chloride, or other hydrocarbons by pyrolysis at temperatures above 70°C (158°F), photolysis, or contact with alkaline materials

—Exposure of trichloroethylene vapors to Hopcalite in a closed environment or to soda lime in closed-circuit anesthesia machines

—Exposure of trichloroethylene liquid to a caustic substance in degreaser tanks

The following methods are effective in controlling worker exposures to dichloroacetylene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dichloroacetylene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and sensory nerves.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dichloroacetylene at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the liver, kidneys, or sensory nerves.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dichloroacetylene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dichloroacetylene on the liver, kidneys, or sensory nerves. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dichloroacetylene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne dichloroacetylene is determined using a solid sorbent (charcoal) tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 1 liter is collected. The sample is then treated with carbon disulfide to extract the dichloroacetylene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If dichloroacetylene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with dichloroacetylene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dichloroacetylene.

A worker who handles dichloroacetylene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dichloroacetylene is handled, processed, or stored.

STORAGE

Dichloroacetylene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must be equipped with explosion-proof electrical equipment and fittings. Containers of dichloroacetylene should be protected from physical damage and should be stored separately from strong acids, oxidizers, potassium, sodium, aluminum powder, heat, sparks, and open flame. Only nonsparking tools may be used to handle dichloroacetylene. An automatic pump should be used to transfer liquid dichloroacetylene from drums or storage containers to process containers. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dichloroacetylene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dichloroacetylene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Isolate the area of the spill or leak.
3. Remove all sources of heat and ignition.
4. If possible to do so without risk, attempt to stop the leak.
5. Ventilate the area of the spill or leak.
6. For small liquid spills, absorb with earth, sand, vermiculite, or other absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes to contain the spill.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dichloroacetylene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dichloroacetylene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dichloroacetylene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dichloroacetylene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dichloroacetylene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves, boots, aprons, and gauntlets should be worn as necessary to prevent prolonged or repeated skin contact with dichloroacetylene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dichloroacetylene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dichloroacetylene.

If dichloroacetylene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dichloroacetylene might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dichloroacetylene. Contact lenses should not be worn when the potential for exposure to dichloroacetylene exists.

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Occupational Health Guideline for o-Dichlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 1,2-$C_6H_4Cl_2$
- Synonyms: 1,2-Dichlorobenzene; o-dichlorobenzol
- Appearance and odor: Colorless to pale yellow liquid with a pleasant aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-dichlorobenzene is a ceiling of 50 parts of o-dichlorobenzene per million parts of air (ppm). This may also be expressed as 300 milligrams of o-dichlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

o-Dichlorobenzene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may also be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: o-Dichlorobenzene vapor may cause irritation of the upper respiratory tract and eyes. Higher concentrations may cause drowsiness, unconsciousness, and death. The liquid may cause burning of the skin. The liquid may also cause burning of the eyes with tissue damage.

2. Long-term Exposure: Prolonged or repeated contact with o-dichlorobenzene may cause skin irritation. Prolonged or repeated inhalation of high concentrations of vapor might cause liver or kidney injury.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to o-dichlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to o-dichlorobenzene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from o-dichlorobenzene exposure.

—Liver disease: o-Dichlorobenzene is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: o-Dichlorobenzene is known as a kidney toxin in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: o-Dichlorobenzene may cause sensitization dermatitis and blistering of the skin . Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

o-Dichlorobenzene vapor at high concentrations is toxic to the liver and kidneys in animals. Rats died from exposure to 977 ppm for 7 hours, but survived when exposed for only 2 hours; animals survived exposure to 539 ppm for 3 hours and at necropsy showed marked centrolobular necrosis of the liver, as well as cloudy swelling of the tubular epithelium of the kidneys. Several species of animals exposed repeatedly to 93 ppm for 7 hours daily showed no adverse effects. The liquid instilled in the rabbit eye produced apparent distress and slight conjunctival irritation. Eye irritation is not

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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usually evident below 20 ppm but becomes noticeable at 25 to 30 ppm and painful to some at 60 to 100 ppm if exposures are for more than a few minutes duration. Some acclimatization may occur, but its extent is not great. Workers exposed daily to an average of 15 ppm showed no indication of injury. The liquid left on the skin may produce blistering. Sensitization dermatitis has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 147
2. Boiling point (760 mm Hg): 180 C (356 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of o-dichlorobenzene): 5.1
5. Melting point: −17.6 C (0.5 F)
6. Vapor pressure at 20 C (68 F): 1.2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers or with hot aluminum or aluminum alloys may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, and carbon monoxide) may be released in a fire involving o-dichlorobenzene.
4. Special precautions: Liquid o-dichlorobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 66 C (151 F) (closed cup)
2. Autoignition temperature: 648 C (1198 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 9.2
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: 2 to 4 ppm, according to the AIHA *Hygienic Guide*; 50 ppm, according to May and Patty.
2. Eye Irritation Level: 20 to 30 ppm according to the AIHA *Hygienic Guide*.
3. Evaluation of Warning Properties: Since the odor threshold of o-dichlorobenzene and the concentration causing eye irritation are at or below the permissible exposure, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of o-dichlorobenzene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure o-dichlorobenzene may be used. An analytical method for o-dichlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6). ical Methods for Set J" (order number PB 263 959).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid o-dichlorobenzene.
- Clothing wet with liquid o-dichlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of o-dichlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-dichlorobenzene, the person performing the operation should be informed of o-dichlorobenzene's hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid o-dichlorobenzene should be removed promptly and not reworn until the o-dichlorobenzene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid o-dichlorobenzene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid o-dichlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any o-dichlorobenzene.
- Employees who handle liquid o-dichlorobenzene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to o-dichlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in cleaning and degreasing of metal, leather, wool, paper, dry cleaning, brick, and upholstery	General dilution ventilation; personal protective equipment
Use as fumigant for poultry houses and stockyards for termites, moths, and beetles	Personal protective equipment
Use in application or removal of surface coatings	General dilution ventilation; personal protective equipment
Use in maintenance of equipment containing heat-transfer agents	Personal protective equipment
Use in organic synthesis in pesticides, herbicides, dyestuffs, and pharmaceuticals; chemical intermediate in manufacture of toluene-diisocyanate and extractive distillation of ethyl benzene from xylene; use as a deodorizing agent	General dilution ventilation
Use in textile dyeing operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid o-dichlorobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid o-dichlorobenzene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid o-dichlorobenzene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of o-dichlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When o-dichlorobenzene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If o-dichlorobenzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.

2. Ventilate area of spill or leak.

3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

o-Dichlorobenzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR o-DICHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
1700 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1700 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for p-Dichlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 1,4-$C_6H_4Cl_2$
- Synonyms: 1,4-Dichlorobenzene; dichlorocide; PDCB
- Appearance and odor: Colorless solid with a moth-ball-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-dichlorobenzene is 75 parts of p-dichlorobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 450 milligrams of p-dichlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Dichlorobenzene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to p-dichlorobenzene may cause irritation of the eyes, nose, and throat. It may also cause headache, swelling around the eyes, and runny nose. In addition, it may cause loss of appetite, nausea, vomiting, weight loss, and liver damage with yellow jaundice and death. Particles of solid p-dichlorobenzene in contact with the eyes may cause pain. The solid material also produces a burning sensation when held in contact with the skin with slight irritation. Warm fumes or strong solutions of p-dichlorobenzene may irritate the skin slightly on prolonged or repeated contact. Red blotching of the skin due to allergy to p-dichlorobenzene may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to p-dichlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-dichlorobenzene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver, respiratory tract, eyes, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Since liver damage has been observed in humans exposed to p-dichlorobenzene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Measurement of 2,5-dichlorophenol may serve as an index of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

p-Dichlorobenzene vapor irritates the eyes and upper respiratory tract and is toxic to the liver. A group of animals repeatedly exposed to 798 ppm developed eye irritation, marked tremors, weakness, and loss of weight; some died. Reversible, nonspecific changes in the eye grounds were noted in rabbits, but there were no lens changes; other effects were centrolobular necrosis of the liver and mild damage to the lungs and kidneys. In five cases of intoxication from exposure to p-dichlorobenzene used as a mothproofing agent, one person with only moderate exposure complained of severe headache, periorbital swelling, and profuse rhinitis, which subsided 24 hours after cessation of exposure.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

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The other four persons who had more prolonged exposure developed anorexia, nausea, vomiting, weight loss, and hepatic necrosis with jaundice; two died, and another developed cirrhosis. In 58 workers exposed for an average of 4.8 years (range, 8 months to 25 years) to p-dichlorobenzene at levels of 10 to 725 ppm, there was no evidence of hematologic effects; painful irritation of the eyes and nose was recorded at levels between 50 and 80 ppm, and it was severe at 160 ppm. Solid particles of p-dichlorobenzene in the human eye cause pain. The solid material produces a burning sensation when held in contact with the skin, but the resulting irritation is slight; warm fumes or strong solutions may irritate the intact skin slightly on prolonged or repeated contact. A case of allergic purpura induced by p-dichlorobenzene has been reported. In a study of workers engaged in synthesizing or otherwise handling p-dichlorobenzene, it was concluded that urinary excretion of 2,5-dichlorophenol (a metabolite of paradichlorobenzene) can serve as an index of exposure. Published studies of tests for carcinogenicity are considered to have been too short in duration and involved too few animals to have any significance.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 147
2. Boiling point (760 mm Hg): 174 C (345 F)
3. Specific gravity (water = 1): 1.46
4. Vapor density (air = 1 at boiling point of p-dichlorobenzene): 5.1
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): 0.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.008
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving p-dichlorobenzene.
4. Special precautions: Liquid p-dichlorobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 65.6 C (150 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 2.5 (calculated at flash point)
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Patty states that "p-dichlorobenzene has a very distinctive aromatic odor. The threshold of detection will vary from 15 to 30 ppm in air. The odor becomes very strong at concentrations between 30 and 60 ppm . . . . It should be recognized, however, that a person may become sufficiently accustomed to the odor to tolerate high concentrations."
2. Irritation Levels: Patty states that p-dichlorobenzene "is painful to the eyes and nose at concentrations of 80 to 160 ppm. Above 160 ppm, it is intolerable to any person who has not worked in it long enough to have had some adaptation."
3. Evaluation of Warning Properties: Through its odor and irritant effects, p-dichlorobenzene can be detected within three times the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure p-dichlorobenzene may be used. An analytical method for p-dichlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid particles or vapors from the surface of hot p-dichlorobenzene.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where p-dichlorobenzene or liquids containing p-dichlorobenzene may contact the eyes.

SANITATION

- Workers subject to skin contact with p-dichlorobenzene should wash any areas of the body which may have contacted p-dichlorobenzene at the end of each work day.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-dichlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Formulation for use in moth control; as a deordorant for garbage and rest rooms; as an insecticide for control of fruit borers and ants; use in organic synthesis for preparation of dye intermediates	General dilution ventilation; local exhaust ventilation; personal protective equipment
Manufacture of p-dichlorobenzene	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application as an insecticide, air deordorant, moth and mildew preventive, and household fumigant	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If p-dichlorobenzene or liquids containing p-dichlorobenzene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If p-dichlorobenzene or liquids containing p-dichlorobenzene get on the skin, wash the contaminated skin using soap or mild detergent and water. If p-dichlorobenzene or liquids containing p-dichlorobenzene penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of p-dichlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When p-dichlorobenzene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If p-dichlorobenzene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dispose in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device as in below or deposit in a secured sanitary landfill.

- Waste disposal methods:

p-Dichlorobenzene may be disposed of:

1. By making packages of p-dichlorobenzene in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-dichlorobenzene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

3. By disposal in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR p-DICHLOROBENZENE

Condition	**Minimum Respiratory Protection* Required Above 75 ppm**
Vapor Concentration	
1,000 ppm or less	A chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and dust filter. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 3,3′-DICHLOROBENZIDINE

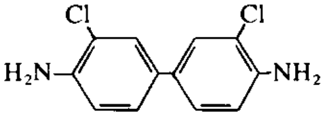
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 3,3′-dichlorobenzidine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_{10}Cl_2N_2$
- **Structure:**



- **Synonyms:** DCB; 4,4′-diamino-3,3′-dichlorobiphenyl; dichlorobenzidine; o,o′-dichlorobenzidine; 3,3′-dichlorobiphenyl-4,4′diamine
- **Identifiers:** CAS 91-94-1; RTECS DD0525000; DOT not assigned.
- **Appearance:** Gray to purple crystalline solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 253.43
2. Melting point: 133 °C (271.4°F)
3. Slightly soluble in water

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, or carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 3,3′-dichlorobenzidine; however, the OSHA standard requires implementation of stringent controls wherever 3,3′-dichlorobenzidine or solid or liquid mixtures containing at least 0.1% by weight or volume of 3,3′-dichlorobenzidine are manufactured, processed, repackaged, released, handled, or stored, (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1007, 3,3′-Dichlorobenzidine (and its salts). The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 3,3′-dichlorobenzidine as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

3,3′-Dichlorobenzidine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of 3,3′-dichlorobenzidine by rats caused irritation and moderate pulmonary congestion. Chronic oral administration of 3,3′-dichlorobenzidine to rats produced gastrointestinal congestion and hemorrhage, leukemia, and cancers of the intestines and mammary and sebaceous glands. Chronic oral administration of 3,3′-dichlorobenzidine produced bladder cancer in hamsters, liver cancer in mice, and liver and bladder cancers in dogs. 3,3′-Dichlorobenzidine exposure to pregnant mice caused an increased incidence of tumors in their offspring.
2. *Effects on humans:* No reports have been identified that associate 3,3′-dichlorobenzidine with the occurrence of cancer in man; however, because 3,3′-dichlorobenzidine and benzidine (a human bladder carcinogen) are usually prepared and handled in the same workplace, 3,3′-dichlorobenzidine may contribute to the incidence of bladder cancer in exposed workers.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 3,3′-dichlorobenzidine can cause allergic skin reaction, dermatitis, headache, and dizziness. It can also cause severe eye irritation and is caustic to the skin.
2. *Long-term (chronic):* Exposure to 3,3′-dichlorobenzidine can cause blood in the urine and painful, difficult, or frequent urination.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 3,3′-dichlorobenzidine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, urinary tract, and hematopoietic (blood-cell-forming) and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 3,3′-dichlorobenzidine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver or urinary tract.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 3,3′-dichlorobenzidine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, urinary tract, and hematopoietic and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The physician should consider use of a test which characterizes internal exposure (e.g., benzidine in urine). However, this test should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 3,3′-dichlorobenzidine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 3,3′-dichlorobenzidine dust with glass-fiber filters and silica gel tubes followed by desorption with triethylamine in methanol and analysis by high-pressure liquid chromatography and ultraviolet detection. Direct-reading devices calibrated to measure 3,3′-dichlorobenzidine may also be used if available. A detailed sampling and analytical method for 3,3′-dichlorobenzidine may be found in the *NIOSH Manual of Analytical Methods* (method number 5509).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 3,3'-dichlorobenzidine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 3,3'-dichlorobenzidine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 3,3'-dichlorobenzidine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 3,3'-dichlorobenzidine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 3,3'-dichlorobenzidine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 3,3'-dichlorobenzidine from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing. OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1007:

Areas where 3,3'-dichlorobenzidine is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers are permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 3,3'-dichlorobenzidine, local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 3,3'-dichlorobenzidine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 3,3'-dichlorobenzidine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 3,3'-dichlorobenzidine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 3,3'-dichlorobenzidine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 3,3′-dichlorobenzidine from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 3,3′-dichlorobenzidine may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 3-3′-dichlorobenzidine

Operations	Controls
During use as an intermediate in the manufacture of dyes, pigments, and isocyanate-containing polymers	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker had contact with 3,3′-dichlorobenzidine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 3,3′-dichlorobenzidine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 3,3′-dichlorobenzidine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 3,3′-dichlorobenzidine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 3,3′-dichlorobenzidine gets on the skin, wash it immediately with soap and water. If 3,3′-dichlorobenzidine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous-air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 3,3′-dichlorobenzidine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 3,3′-dichlorobenzidine may be collected and placed in an appropriate container.
3. 3,3′-Dichlorobenzidine solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of 3,3′-dichlorobenzidine are prohibited by OSHA.
4. For small quantities of liquids containing 3,3′-dichlorobenzidine, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing 3,3′-dichlorobenzidine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 3-3′-dichlorobenzidine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Dichlorodifluoromethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CCl_2F_2
- Synonyms: Refrigerant 12; Freon 12; propellant 12; Halon 122
- Appearance and odor: Colorless gas with a characteristic ether-like odor that is detectable only in concentrations well above the permissible exposure (above 20% by volume).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dichlorodifluoromethane is 1000 parts of dichlorodifluoromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4950 milligrams of dichlorodifluoromethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dichlorodifluoromethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to dichlorodifluoromethane may cause dizziness, involuntary trembling, unconsciousness, and death. It may also cause irregular heartbeat. If the liquid gets on the skin or in the eyes, it may cause frostbite.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dichlorodifluoromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dichlorodifluoromethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from dichlorodifluoromethane exposure.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of dichlorodifluoromethane might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Dichlorodifluoromethane vapor is a narcotic and can cause asphyxia at very high concentrations. At 800,000 ppm rats were deeply anesthetized, but 4 to 6 hours' exposure produced no permanent effects. At 200,000 ppm dogs and monkeys showed only tremors, salivation, and lacrimation. Inhalation by man at 150,000 ppm produces unconsciousness, while dizziness occurs at 50,000 ppm. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest, probably due to sensitization of the myocardium. In liquid form this substance may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 120.9
  2. Boiling point (760 mm Hg): −29.8 C (−21.6 F)
  3. Specific gravity (water = 1): 1.49 (at boiling

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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point)

4. Vapor density (air = 1 at boiling point of dichlorodifluoromethane): 4.2

5. Melting point: −157.7 C (−252 F)

6. Vapor pressure at 20 C (68 F): 5.7 atm.

7. Solubility in water, g/100 g water at 20 C (68 F): 0.008

8. Evaporation rate (butyl acetate = 1): 380

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Dichlorodifluoromethane reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when dichlorodifluoromethane decomposes.

4. Special precautions: Liquid dichlorodifluoromethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Since dichlorodifluoromethane is practically odorless and is not an irritant, it is treated as a material with poor warning properties.

Grant states that "in ordinary occupational or domestic exposure to the gas, there is neither ocular nor respiratory irritation. Dogs, monkeys, and guinea pigs exposed to 20% of the gas in air for several hours a day for several days showed temporary intoxication with tremors, ataxia, and associated tendency to stare, salivate, and lacrimate, but no cumulative toxic effect and no specific ocular disturbance. The speed of reflex closure of the eyes is such that it seems extremely unlikely that any seriuos injury would result from an accidental spray of this substance in the eyes of human beings."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for dichlorodifluoromethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming wet with liquid dichlorodifluoromethane or from becoming frozen from contact with vessels containing dichlorodifluoromethane.
- Any clothing which becomes wet with liquid dichlorodifluoromethane should be removed immediately and not reworn until the dichlorodifluoromethane has evaporated from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dichlorodifluoromethane may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dichlorodifluoromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of aerosols for cosmetics,	General dilution ventilation; personal

pharmaceuticals, insecticides, paints, adhesives, and cleaners; use in manufacture and extensive use as a refrigerant in home and commercial applications	protective equipment
Use as a blowing agent for cellular polymers; use as a solvent or diluent in fumigants for food sterilization; in paints and varnish removers, and in polymerization processes	General dilution ventilation; personal protective equipment
Use as a foaming agent in fire extinguishing, aerosols, for surfactants; use in Immersion Quick Freezing of food products	General dilution ventilation; personal protective equipment
Use in water purification; copper and aluminum purification, petroleum recovery, and in manufacture of glass bottles	General dilution ventilation; personal protective equipment
Use in regulating devices for leak detection; in thermal expansion valves; use in manufacture of materials for electrical applications as insulators and generator windings	General dilution ventilation; personal protective equipment
Use in organic synthesis of Freons, and a polymerization catalysts; use as a working fluid for heat pumps and in hydraulic fluids	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid dichlorodifluoromethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dichlorodifluoromethane gets on the skin, immediately flush the skin with water if the dichlorodifluoromethane has not already evaporated. If liquid dichlorodifluoromethane soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for flushing. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of dichlorodifluoromethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If dichlorodifluoromethane is leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. Stop flow of gas.

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RESPIRATORY PROTECTION FOR DICHLORODIFLUOROMETHANE

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,3-Dichloro-5,5-Dimethylhydantoin

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_5H_6Cl_2N_2O_2$
- Synonyms: Halane; dactin
- Appearance and odor: White solid with a chlorine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,3-dichloro-5,5-dimethylhydantoin is 0.2 milligram of 1,3-dichloro-5,5-dimethylhydantoin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,3-Dichloro-5,5-dimethylhydantoin can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: This chemical is a chlorine bleach which is activated by moisture and may irritate the eyes, nose, throat, lungs, and skin.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,3-dichloro-5,5-dimethylhydantoin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,3-dichloro-5,5-dimethylhydantoin at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,3-dichloro-5,5-dimethylhydantoin exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,3-dichloro-5,5-dimethylhydantoin might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,3-Dichloro-5,5-dimethylhydantoin powder in contact with water yields hypochlorous acid, which is an eye and mucous membrane irritant. The LD50 for rats, when administered orally as a 10% aqueous suspension, was 542 mg/kg; at necropsy, gastrointestinal hemorrhages were found. There is a single report of workmen exposed to an average concentration of 1.97 mg/m^3 experiencing marked respiratory irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 197
2. Boiling point (760 mm Hg): Not available
3. Specific gravity (water = 1): 1.5
4. Vapor density (air = 1 at boiling point of 1,3-dichloro-5,5-dimethylhydantoin): 6.8
5. Melting point: 130 C (266 F)
6. Vapor pressure at 20 C (68 F): Not available
7. Solubility in water, g/100 g water at 20 C (68 F): 0.20
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Dry 1,3-

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dichloro-5,5-dimethylhydantoin decomposes with formation of toxic gases at 202 – 210 C (395 – 410 F). If material is wet, it will decompose at lower temperatures.

2. Incompatibilities: Contact with water, strong acids, and easily oxidized materials such as ammonium salts, sulfides, etc., may cause fires and explosions and formation of toxic fumes of chlorine and nitrogen trichloride.

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine, hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,3-dichloro-5,5-dimethylhydantoin.

4. Special precautions: 1,3-Dichloro-5,5-dimethylhydantoin will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 174 C (346 F)
2. Autoignition temperature: Not available
3. Flammable limits in air, % by volume: Not available
4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

1,3-Dichloro-5,5-dimethylhydantoin is a powder, but in the presence of moisture chlorine gas is released. May states that the odor threshold of chlorine is .01 ppm, which is well below the permissible exposure of 1 ppm. Chlorine has adequate warning properties.

Stecher reports that the chlorine liberated upon the decomposition of 1,3-dichloro-5,5-dimethylhydantoin may produce irritation of the eyes and mucous membranes. Patty reports that men can work without interruption in an environment containing 3 to 6 mg/m^3 of chlorine, but exposures to concentrations of 10 to 20 mg/m^3 causes "a stinging or burning sensation in the eyes . . . ." Eye protection is recommended for any possibility of contact in the personal protection section.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for 1,3-dichloro-5,5-dimethylhydantoin had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin.
- If employees' clothing may have become contaminated with solid 1,3-dichloro-5,5-dimethylhydantoin, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,3-dichloro-5,5-dimethylhydantoin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,3-dichloro-5,5-dimethylhydantoin, the person performing the operation should be informed of 1,3-dichloro-5,5-dimethylhydantoin's hazardous properties.
- Non-impervious clothing which becomes contaminated with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should be removed promptly and not reworn until the 1,3-dichloro-5,5-dimethylhydantoin is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should be promptly washed or showered with soap or mild detergent and water to remove any 1,3-dichloro-5,5-dimethylhydantoin.
- Employees who handle solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,3-dichloro-5,5-dimethylhydantoin may occur and control methods which may be effective in each case:

Operation	Controls
Use as a bactericide, sporicide, or sanitizer in swimming pools, dairies, laundries, restaurants, cutting oils, and pharmaceutical industry; as a general cleaner	General dilution ventilation; personal protective equipment
Use as a mild chlorinating agent in organic synthesis	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during use as a rubber retarder	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a bleaching agent in commercial laundries	General dilution ventilation; personal protective equipment
Use as stabilizer, discoloration preventer, and catalyst in polymer industry; use to emboss or texturize resinous sheet preparations	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,3-dichloro-5,5-dimethylhydantoin gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin get on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If liquids containing 1,3-dichloro-5,5-dimethylhydantoin soak through the clothing, remove the clothing promptly and flush the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,3-dichloro-5,5-dimethylhydantoin, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,3-dichloro-5,5-dimethylhydantoin has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If 1,3-dichloro-5,5-dimethylhydantoin is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood.) Small quantities may also be slowly added to large amounts of water and flushed into a sewer. Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

1,3-Dichloro-5,5-dimethylhydantoin may be disposed of:

1. By making packages of 1,3-dichloro-5,5-dimethylhydantoin in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving 1,3-dichloro-5,5-dimethylhydantoin in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

3. Small quantities may be slowly added to large amounts of water and flushed into a sewer.

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RESPIRATORY PROTECTION FOR 1,3-DICHLORO-5,5-DIMETHYLHYDANTOIN

Condition	**Minimum Respiratory Protection* Required Above 0.2 mg/m^3**
Particulate Concentration	
5 mg/m^3 or less	Any chemical cartridge respirator with a full facepiece, chlorine cartridge(s), and dust filter(s).
	A gas mask with a chin-style or a front- or back-mounted chlorine canister and dust filter.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 5 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against chlorine and particulates.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,1-Dichloroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3CHCl_2
- Synonyms: Asymmetrical dichloroethane; ethylidene chloride; 1,1-ethylidene dichloride
- Appearance and odor: Colorless liquid with a chloroform-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1-dichloroethane is 100 parts of 1,1-dichloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 400 milligrams of 1,1-dichloroethane per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for 1,1-dichloroethane a Threshold Limit Value of 200 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1-Dichloroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Breathing 1,1-dichloroethane vapor may cause drowsiness and unconsciousness. It might also cause damage to the liver, kidneys, and lungs. Splashing the liquid in the eyes may cause irritation.

2. Long-term Exposure: Prolonged, confined, or repeated skin contact with 1,1-dichloroethane can produce a slight burn.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1-dichloroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1-dichloroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1-dichloroethane exposure.

—Skin disease: 1,1-Dichloroethane can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although 1,1-dichloroethane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although 1,1-dichloroethane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,1-dichloroethane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,1-Dichloroethane vapor is a narcotic. Rats exposed to 32,000 ppm for 30 minutes did not survive. The most consistent findings in animals exposed to concentrations

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of above 8,000 ppm for up to 7 hours were pathologic changes in the kidney and liver, and at much higher concentrations, near 64,000 ppm, damage to the lungs as well. Repeated daily exposure of several species of animals to 1,000 ppm resulted in no pathologic or hematologic changes. The liquid applied to the intact or abraded skin of rabbits produced slight edema and very slight necrosis after six daily applications. Instilled in the eyes of rabbits there was immediate, moderate conjunctival irritation and swelling which subsided within a week. There have been no reported cases of human overexposure by inhalation; prolonged, confined, or repeated skin contact can produce a slight burn.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 99
2. Boiling point (760 mm Hg): 57.3 C (135 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 1,1-dichloroethane): 3.4
5. Melting point: −96.7 C (−142 F)
6. Vapor pressure at 20 C (68 F): 182 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): 11.6

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong caustics will cause formation of flammable and toxic acetaldehyde gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as vinyl chloride, hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,1-dichloroethane.
4. Special precautions: 1,1-Dichloroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −8.5 C (17 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 5.9; Upper: 15.9
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

The AIHA *Hygienic Guide* reports that 1,1-dichloroethane has a distinctive, easily recognizable odor at the TLV.

1,1-Dichloroethane is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1-dichloroethane may be used. An analytical method for 1,1-dichloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1-dichloroethane.
- Clothing wet with liquid 1,1-dichloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dichloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1-dichloroethane, the person performing the operation should be informed of 1,1-dichloroethane's hazardous properties.
- Any clothing which becomes wet with liquid 1,1-dichloroethane should be removed immediately and not

reworn until the 1,1-dichloroethane is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1-dichloroethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 1,1-dichloroethane should be immediately washed or showered with soap or mild detergent and water to remove any 1,1-dichloroethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1-dichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as dewaxer of mineral oils; extractant for heat-sensitive substances	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a fumigant	General dilution ventilation of work area; personal protective equipment
Use in manufacture of vinyl chloride by vapor phase cracking; use in manufacture of high vacuum rubber and silicon grease; use as a chemical intermediate	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,1-dichloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1-dichloroethane gets on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If 1,1-dichloroethane soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1-dichloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1-dichloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1-dichloroethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. 1,1-Dichloroethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of 1,1-dichloroethane vapors are permitted.

- Waste disposal method:

1,1-Dichloroethane may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR 1,1-DICHLOROETHANE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,2-Dichloroethylene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ClCH=CHCl
- Synonyms: Acetylene dichloride; dioform; trans-acetylene dichloride; sym-dichloroethylene
- Appearance and odor: Colorless liquid with an ether-like, slightly acrid odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,2-dichloroethylene is 200 parts of 1,2-dichloroethylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 790 milligrams of 1,2-dichloroethylene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,2-Dichloroethylene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to 1,2-dichloroethylene may cause dizziness, drowsiness, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,2-dichloroethylene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,2-dichloroethylene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,2-dichloroethylene exposure.

—Liver disease: Although 1,2-dichloroethylene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,2-dichloroethylene might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,2-Dichloroethylene vapor is a narcotic and a mucous-membrane irritant. Variations in toxicity of the cis- as compared with the trans-form have been reported. A concentration of 39,000 ppm was lethal to guinea pigs, and narcosis was produced at 18,000 ppm. Dogs exposed to high concentrations of vapor developed superficial corneal turbidity which was reversible. No effects were observed in several species with repeated exposure for up to 6 months at 1000 ppm. It has been used as a general anesthetic in man; one industrial fatality was due to very high vapor inhalation in a small enclosure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 96.9
2. Boiling point (760 mm Hg): 45 to 60 C (113 to 140 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of 1,2-dichloroethylene): 3.34
5. Melting point: −49 to −81.5 C (−56 to −115 F)
6. Vapor pressure at 20 C (68 F): 180 to 265 mm Hg

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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7. Solubility in water, g/100 g water at 20 C (68 F): 0.35 to 0.63

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,2-dichloroethylene.

4. Special precautions: 1,2-Dichloroethylene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 2.2 to 3.9 C (36 to 39 F) (closed cup)

2. Autoignition temperature: 460 C (860 F) for trans-1,2-dichloroethylene

3. Flammable limits in air, % by volume: Lower: 9.7; Upper: 12.8

4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

May reports an odor threshold of 0.085 ppm for dichloroethylene. For the purposes of this guideline, 1,2-dichloroethylene is treated as a material with adequate warning properties.

1,2-Dichloroethylene is an eye irritant, according to Grant, but the concentrations at which irritation occurs are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of 1,2-dichloroethylene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,2-dichloroethylene may be used. An analytical method for 1,2-dichloroethylene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,2-dichloroethylene.
- Clothing wet with liquid 1,2-dichloroethylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,2-dichloroethylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,2-dichloroethylene, the person performing the operation should be informed of 1,2-dichloroethylene's hazardous properties.
- Any clothing which becomes wet with liquid 1,2-dichloroethylene should be removed immediately and not reworn until the 1,2-dichloroethylene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,2-dichloroethylene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 1,2-dichloroethylene should be promptly washed or showered with soap or mild detergent and water to remove any 1,2-dichloroethylene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,2-dichloroethylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a low-temperature solvent for heat-sensitive substances in extraction of caffeine, perfume oils, and fats from flesh of animals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber and dye industries in extraction and application	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a direct solvent in gums, waxes, oils, camphor, and phenol; use in solvent mixtures for esters and ether derivatives, lacquers, resins, thermoplastics, and artificial fibers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for polymers and telomers	Process enclosure; local exhaust ventilation; personal protective equipment
Use in miscellaneous applications as liquid dry cleaning agent, cleaning solution for printed circuit boards, food packaging adhesives, and germicidal fumigants	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,2-dichloroethylene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,2-dichloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,2-dichloroethylene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,2-dichloroethylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,2-dichloroethylene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,2-dichloroethylene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. 1,2-Dichloroethylene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of 1,2-dichloroethylene vapors are permitted.

- Waste disposal method:

1,2-Dichloroethylene may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR 1,2-DICHLOROETHYLENE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dichloroethyl Ether

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(ClCH_2CH_2)_2O$
- Synonyms: Bis(2-chloroethyl)ether;2,2'-dichlorodiethyl ether
- Appearance and odor: Colorless liquid with a chlorinated solvent-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dichloroethyl ether is a ceiling level of 15 parts of dichloroethyl ether per million parts of air (ppm). This may also be expressed as 90 milligrams of dichloroethyl ether per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for dichloroethyl ether a Threshold Limit Value of 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dichloroethyl ether can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to dichloroethyl ether vapor may cause severe irritation of the eyes and nose with coughing, retching, and nausea. In animal experiments, dichloroethyl ether has caused severe irritation of the respiratory tract with severe breathing difficulties which can be delayed in onset. Animal experiments have also shown dichloroethyl ether vapor to be capable of causing drowsiness, dizziness, and unconsciousness at high concentrations. Liquid dichloroethyl ether placed in animal eyes has produced damage. Feeding this chemical to mice has been associated with an increased amount of liver tumors.

2. Long-term Exposure: Repeated exposure to dichloroethyl ether may cause bronchitis.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dichloroethyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dichloroethyl ether at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory tract, liver, and the central nervous system should be stressed.

—14" x 17" chest roentgenogram: Dichloroethyl ether causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Dichloroethyl ether is a severe pulmonary irritant in animals. Periodic surveillance is indicated.

2. Periodic Medical Examination: The above medical examinations are to be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or signs and symptoms of respiratory disease.

- **Summary of toxicology**

Dichloroethyl ether vapor is a severe respiratory irritant; high levels cause narcosis in animals. It is tumorigenic in animals. Repeated oral administration of 100 mg/kg daily to both sexes of two strains of mice for 80 weeks induced a significantly elevated incidence of tumors, mostly hepatomas. In guinea pigs, concentrations of 500 to 1000 ppm were fatal after 5 to 8 hours of

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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exposure; there were immediate lacrimation and nasal irritation, followed by unsteadiness and coma; autopsy findings were pulmonary edema, hemorrhage and occasional complete consolidation. In experimental human exposure, 500 ppm caused intolerable irritation to the eyes and nose with cough, nausea and vomiting; at 100 ppm there was some irritation, while at 35 ppm there were no effects. Except for accidental inhalation of high concentrations, the chief hazard in industrial practice is mild bronchitis, which may be caused by repeated exposures to low concentrations. Both the liquid and a 10% solution dropped in the eye of a rabbit caused moderate discomfort, conjunctival irritation, and corneal injury which generally healed within 24 hours. On the skin of rabbits, the pure liquid had no local effect, but a sufficient amount penetrated the skin to cause death within a day.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 143
2. Boiling point (760 mm Hg): 178.2 C (353 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of dichloroethyl ether): 4.9
5. Melting point: −52 C (−62 F)
6. Vapor pressure at 20 C (68 F): 0.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.1
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: At elevated temperatures containers may burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving dichloroethyl ether.
4. Special precautions: Dichloroethyl ether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 55 C (131 F) (closed cup)
2. Autoignition temperature: 369 C (696 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: According to Patty, "most people can detect the chemical at its threshold limit (15 ppm) by its odor."
2. Irritation Levels: Patty states that "Schrenk, Patty, and Yant exposed human volunteers to dichloroethyl ether. Brief exposure to concentrations above 550 ppm were very irritating to the eyes and nasal passages and were considered intolerable. They also caused coughing, retching, and nausea. At 260 and 100 ppm the irritating effects were still present to some extent but were not considered intolerable."
3. Evaluation of Warning Properties: Through its odor dichloroethyl ether can be detected at the permissible exposure limit. For the purposes of this guideline, therefore, dichloroethyl ether is treated as a substance with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of dichloroethyl ether. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dichloroethyl ether may be used. An analytical method for dichloroethyl ether is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid dichloroethyl ether, where skin contact may occur.
- Clothing contaminated with dichloroethyl ether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dichloroethyl ether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dichloroethyl ether, the person performing the operation should be informed of dichloroethyl ether's hazardous properties.
- Where exposure of an employee's body to liquid dichloroethyl ether may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with dichloroethyl ether should be removed immediately and not reworn until the dichloroethyl ether is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dichloroethyl ether may contact the eyes.

SANITATION

- Skin that becomes contaminated with dichloroethyl ether should be immediately washed or showered with soap or mild detergent and water to remove any dichloroethyl ether.
- Employees who handle dichloroethyl ether should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dichloroethyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as solvent, dewaxing agent in petroleum industry and manufacture of oils, fats, waxes, gums, tars, resins, soaps, ethyl cellulose, paints, varnish, and lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as scouring and penetrating agent in textile industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as fumigant in agricultural insecticide industry	Personal protective equipment
Use as chemical intermediate in synthesis during manufacture of pharmaceuticals, rubber chemicals, resins, plasticizers, and chemicals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as lead scavenger during production of gasoline engine anti-knock compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid dichloroethyl ether gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dichloroethyl ether gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid dichloroethyl ether soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of dichloroethyl ether, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid dichloroethyl ether has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dichloroethyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Dichloroethyl ether should not be allowed to enter a confined space, such as sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of dichloroethyl ether vapors are permitted.

- Waste disposal methods:

Dichloroethyl ether may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on dichloroethyl ether, look up dichloroethyl ether in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 9, 1975.

RESPIRATORY PROTECTION FOR DICHLOROETHYL ETHER

Condition	Minimum Respiratory Protection* Required Above 15 ppm
Vapor Concentration	
150 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
250 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 250 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dichloroethyl ether; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 250 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Dichloromonofluoromethane (Refrigerant 21)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CHCl_2F$
- Synonyms: Refrigerant 21; Freon 21; Halon 112; dichlorofluoromethane
- Appearance and odor: Colorless liquid or gas with a slight ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Refrigerant 21 is 1000 parts of Refrigerant 21 per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4200 milligrams of Refrigerant 21 per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Refrigerant 21 can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to Refrigerant 21 may cause drowsiness, unconsciousness, and death. Exposure to Refrigerant 21 may cause the heart to beat irregularly. If the liquid is spilled on the skin, it may cause frostbite.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Refrigerant 21.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Refrigerant 21 at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from Refrigerant 21 exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Refrigerant 21 might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of Refrigerant 21 might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Refrigerant 21 vapor is a respiratory irritant and causes asphyxia at extremely high concentrations. Exposure to 400,000 ppm with 18% oxygen was fatal to guinea pigs; death was preceded by dyspnea, tremors, and convulsive movements but not narcosis. Animals died at 102,000 ppm with congested lungs, kidneys, and liver, but survived 52,000 ppm showing tremors, incoordination, and irregular breathing. In liquid form this substance may cause frostbite. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest, probably due to sensitization of the myocardium. Acute or chronic effects from human exposure have not been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.9

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Boiling point (760 mm Hg): 8.9 C (48.1 F)
3. Specific gravity (water = 1): 1.37
4. Vapor density (air = 1 at boiling point of Refrigerant 21): 3.82
5. Melting point: −135 C (−211 F)
6. Vapor pressure at 20 C (68 F): Data not available
7. Solubility in water, g/100 g water at 20 C (68 F): 1
8. Evaporation rate (butyl acetate = 1): Much higher than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Refrigerant 21 reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when Refrigerant 21 decomposes.
4. Special precautions: Liquid Refrigerant 21 will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Since there is no available quantitative information relating warning properties to air concentrations of Refrigerant 21, this substance is treated as a material with poor warning properties.

Refrigerant 21 is not a known eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for Refrigerant 21 is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming wet with liquid Refrigerant 21.
- Any clothing which becomes wet with liquid Refrigerant 21 should be removed immediately and not reworn until the Refrigerant 21 has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid Refrigerant 21 may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Refrigerant 21 may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and use as an aerosol propellant in pharmaceuticals; use as a refrigerating agent; use as an industrial solvent in separation of fatty acids, of polymers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a blowing agent for rigid foams and insulating foams	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a working fluid in Rankine cycle turbogenerators; use in water purification; use in organic synthesis in preparation of other Freons	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid Refrigerant 21 gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid Refrigerant 21 gets on the skin, immediately flush the contaminated skin with water if the Refrigerant 21 has not already evaporated. If liquid Refrigerant 21 soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of Refrigerant 21, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When Refrigerant 21 has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Refrigerant 21 is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow.
3. If the liquid is spilled or leaked, allow to vaporize.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Dichloromonofluoromethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR REFRIGERANT 21

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,1-Dichloro-1-Nitroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CCl_2NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with an unpleasant odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1-dichloro-1-nitroethane is a ceiling of 10 parts of 1,1-dichloro-1-nitroethane per million parts of air (ppm). This may also be expressed as 60 milligrams of 1,1-dichloro-1-nitroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1-Dichloro-1-nitroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure of animals has produced severe irritation of the lungs with severe breathing difficulties. These breathing difficulties may be delayed in onset. Liver, heart, kidney, and blood vessel damage were also reported in animals. In addition, eye and skin irritation have been reported in animals.

- **Reporting Signs and Symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1-dichloro-1-nitroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1-dichloro-1-nitroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1-dichloro-1-nitroethane exposure.

—Chronic respiratory disease: 1,1-Dichloro-1-nitroethane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,1-dichloro-1-nitroethane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 1,1-Dichloro-1-nitroethane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 1,1-Dichloro-1-nitroethane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: 1,1-Dichloro-1-nitroethane causes heart damage in animals. In persons with impaired cardiovascular function, the inhalation of 1,1-dichloro-1-nitroethane might cause exacerbation of preexisting disorders.

—Skin disease: 1,1-Dichloro-1-nitroethane can cause dermatitis on prolonged exposure. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,1-Dichloro-1-nitroethane vapor is a pulmonary, skin, and eye irritant in animals. It also causes liver, kidney, and heart damage in animals. At high concentrations animals showed lacrimation, increased nasal secretion,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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sneezing, coughing, pulmonary rales, and weakness. Exposure of rabbits to levels as low as 52 ppm for 18-½ hours was fatal. Autopsies on animals exposed to more than 170 ppm for over 30 minutes revealed pulmonary edema and hemorrhage, with damage to the heart, liver, and kidneys. Application of the liquid to the skin of rabbits caused irritation and edema. No human experience has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 144
2. Boiling point (760 mm Hg): 125 C (257 F)
3. Specific gravity (water = 1): 1.42
4. Vapor density (air = 1 at boiling point of 1,1-dichloro-1-nitroethane): 5.0
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 15 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.25
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Overheating in closed containers may cause explosions.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, hydrogen chloride, and carbon monoxide) may be released in a fire involving 1,1-dichloro-1-nitroethane.
4. Special precautions: Liquid 1,1-dichloro-1-nitroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 58 C (136 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of 1,1-dichloro-1-nitroethane.
2. Eye Irritation Level: The *Handbook of Organic Industrial Solvents* states that this substance "may cause irritation of eyes and nose at twice threshold limit and, at higher concentrations, lung injury." Grant points out that it "has an irritant, lacrimogenic effect which gives adequate warning to prevent dangerous exposure."
3. Evaluation of Warning Properties: Although 1,1-dichloro-1-nitroethane produces irritant effects at only twice the permissible exposure limit, it is treated as a substance with poor warning properties, since the permissible exposure limit is a ceiling concentration which was set "to prevent serious injury in man."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of 1,1-dichloro-1-nitroethane. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1-dichloro-1-nitroethane may be used. An analytical method for 1,1-dichloro-1-nitroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1-dichloro-1-nitroethane.

- Clothing wet with liquid 1,1-dichloro-1-nitroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dichloro-1-nitroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1-dichloro-1-nitroethane, the person performing the operation should be informed of 1,1-dichloro-1-nitroethane's hazardous properties.
- Non-impervious clothing which becomes contaminated with 1,1-dichloro-1-nitroethane should be removed promptly and not reworn until the 1,1-dichloro-1-nitroethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1-dichloro-1-nitroethane may contact the eyes.

SANITATION

- Skin that becomes contaminated with 1,1-dichloro-1-nitroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1-dichloro-1-nitroethane.
- Employees who handle liquid 1,1-dichloro-1-nitroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1-dichloro-1-nitroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as an insecticidal fumigant for grain (this product is not in common use at this time)	Material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid 1,1-dichloro-1-nitroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid 1,1-dichloro-1-nitroethane gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid 1,1-dichloro-1-nitroethane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1-dichloro-1-nitroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid 1,1-dichloro-1-nitroethane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid 1,1-dichloro-1-nitroethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. 1,1-Dichloro-1-nitroethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

1,1-Dichloro-1-nitroethane may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR 1,1-DICHLORO-1-NITROETHANE

Condition	**Minimum Respiratory Protection* Required Above 10 ppm**
Vapor Concentration	
150 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 150 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 1,3-DICHLOROPROPENE

INTRODUCTION

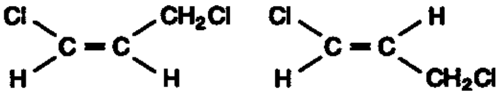
This guideline summarizes pertinent information about 1,3-dichloropropene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_4Cl_2$

- **Structure**



- **Synonyms**

alpha-Chloroallyl chloride; gamma-chloroallyl chloride; 1,3-dichloropropylene; 1,3-dichloropropene-1; Telone; Telone II; Dorlone; alpha,gamma-dichloropropylene.

- **Identifiers**

1. CAS No.: 542-75-6
2. RTECS No.: UC8310000
3. DOT UN: 2047 29
4. DOT label: Flammable liquid

- **Appearance and odor**

1,3-Dichloropropene is a straw-colored liquid with a chloroform-like odor; the commercial product consists of the cis- and trans-isomers in approximately equal parts.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110.98
2. Boiling point (760 mm Hg): 103°C (217°F)
3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
4. Vapor density at 37.8°C (100°F): 3.8
5. Freezing point: -84°C (-119.2°F)
6. Vapor pressure at 25°C (77°F): approximately 28 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Insoluble in water; soluble in acetone, toluene, octane, carbon tetrachloride, n-heptane, methanol, and benzene.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. The vapors of this substance also form explosive mixtures with air.

2. Incompatibilities: Contact of 1,3-dichloropropene with oxidizers, aluminum or magnesium compounds, or alkaline or corrosive materials causes a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 1,3-dichloropropene.

4. Special precautions: This substance can polymerize if not stabilized with epichlorohydrin or another stabilizer.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to 1,3-dichloropropene.

1. Flash point: 35°C (95°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 5.3; upper, 14.5

4. Extinguishant: Use water spray, dry chemical, standard foam, or carbon dioxide to fight fires involving 1,3-dichloropropene. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving 1,3-dichloropropene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of 1,3-dichloropropene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 1,3-dichloropropene. Structural firefighters' protective clothing may provide limited protection against fires involving 1,3-dichloropropene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 1,3-dichloropropene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (5 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure. However, 1,3-dichloropropene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 1,3-dichloropropene a threshold limit value (TLV) of 1 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 1,3-dichloropropene [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer associated with 1,3-dichloropropene exposure. The ACGIH limit is based on the risk of kidney injury associated with exposure to 1,3-dichloropropene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 1,3-dichloropropene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to 1,3-dichloropropene irritates the skin, eyes, and mucous membranes and may cause respiratory tract, liver, and kidney damage in experimental animals. 1,3-Dichloropropene is also carcinogenic in rodents. Exposure to 1,3-dichloropropene vapor (concentration and duration not specified) caused moderate to severe conjunctival irritation and slight to moderate reversible corneal injury in rabbits; applied to the skin of animals of the same species, this substance caused swelling and necrosis [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits for the same solution is 504 mg/kg [ACGIH 1991]. The LC_{50} in rats is 500 ppm for an unspecified period of time, while the 2-hr LC_{50} in mice is 1,033 ppm [NIOSH 1993]. The oral LD_{50} for a 10-percent solution of 1,3-dichloropropene (92-percent purity) in corn oil is 713 mg/kg in male rats and 470 mg/kg in female rats [ACGIH 1991]. Acute inhalation exposure (duration not specified) to concentrations above 2,700 ppm irritated the eyes and nose and caused serious injury to the lungs, liver, and kidneys of rats; exposure to a 1,000 ppm concentration for a period described as "brief" caused severe eye irritation and loss of consciousness, while exposure to 1,000 ppm for 2 hours was lethal to all exposed rats [ACGIH 1991]. Exposure to a 3 ppm concentration of 1,3-dichloropropene for 7-hours a day, 5 days a week for 6 months produced reversible swelling of renal tubular epithelium in rats [ACGIH 1991]. Rats and mice exposed to 0, 93, 32, or 12 ppm for 7 hours a day, 5 days a week for 13 weeks experienced growth depression (high dose rats and female mice) and focal changes of the nasal epithelium in high dose rats (both sexes) and female rats exposed to 32 ppm [Clayton and Clayton 1981]. 1,3-Dichloropropene has been tested in oral carcinogenicity bioassays in both mice and rats. In mice, it produced dose-related increases in the incidences of benign and/or malignant tumors of the urinary bladder, lung, and forestomach. In male rats, it caused dose-related increases in the incidences of benign and malignant forestomach tumors and benign liver tumors; in female rats, it produced benign forestomach tumors [IARC 1986]. Based on this evidence, the International Agency for Research on Cancer has concluded that the evidence for the carcinogenicity of technical-grade 1,3-dichloropropene in animals is sufficient [IARC 1986].

2. *Effects on Humans:* Exposure to 1,3-dichloropropene irritates the eyes, skin, and mucous membranes and may produce respiratory damage in humans. Prolonged skin contact with this substance may cause burns or an itching, red rash [NLM 1992]. After an explosion of a tank car containing this substance, exposed workers immediately experienced coughing and choking, followed by headache, dizziness, irritation of the mucous membranes, and chest discomfort; three of the exposed workers lost consciousness and subsequently died. Pulmonary effects included atelectasis, emphysema, pneumonia, and pulmonary edema [Gosselin et al. 1984]. Individuals exposed to 1,3-dichloropropene during a spill reported headache, fatigue, irritation of the mucous membranes, chest pain, and abdominal discomfort that persisted for up to 2 weeks [Gosselin et al. 1984]. Two firemen previously treated for acute symptoms after exposure to 1,3-dichloropropene subsequently developed malignant histiocytic lymphomas [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 1,3-dichloropropene include pain, redness, and tearing of the eyes; redness and inflammation of the eyelids; redness, burns, and rashes of the skin; headache; fatigue; loss of consciousness; coughing; shortness of breath; chest discomfort; abdominal discomfort; and vomiting. In addition, two cases of malignant histiocytic lymphoma have been reported in workers acutely overexposed to this substance.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to 1,3-dichloropropene include skin burns and cracked, rough, and reddened skin.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of 1,3-dichloropropene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 1,3-dichloropropene or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200)]. All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 1,3-dichloropropene and lead to worker exposures to this substance:

—Use as a soil fumigant

—Use as a chemical intermediate

The following methods are effective in controlling worker exposures to 1,3-dichloropropene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to 1,3-dichloropropene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 1,3-dichloropropene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 1,3-dichloropropene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 1,3-dichloropropene on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 1,3-dichloropropene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 1,3-dichloropropene is made using a charcoal solid sorbent tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 5 liters is collected. The sample is then treated with carbon disulfide to extract the 1,3-dichloropropene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in NIOSH Method No. 1003 in the *NIOSH Analytical Methods Manual* [NIOSH 1984], which has been modified for use by OSHA.

PERSONAL HYGIENE

1,3-Dichloropropene can be absorbed through the skin in toxic amounts. Therefore, if 1,3-dichloropropene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with 1,3-dichloropropene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of 1,3-dichloropropene, particularly its ability to be absorbed through the skin in toxic amounts.

A worker who handles 1,3-dichloropropene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 1,3-dichloropropene is handled, processed, or stored.

STORAGE

1,3-Dichloropropene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Electrical equipment in storage areas must meet requirements for OSHA Class I flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of 1,3-dichloropropene should be protected from physical damage and should be stored separately from oxidizers, aluminum or magnesium compounds, alkaline or corrosive materials, and heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle 1,3-dichloropropene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained 1,3-dichloropropene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 1,3-dichloropropene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the 1,3-dichloropropene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  1,3-Dichloropropene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for 1,3-dichloropropene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center *immediately* at

(202) 426-2675 or at (800) 424-8802 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of 1,3-dichloropropene per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 1,3-dichloropropene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. 1,3-Dichloropropene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.]* and has been assigned EPA Hazardous Waste No. U084. This chemical is approved for land disposal as long as the concentration of 1,3-dichloropropene in the waste or treatment residual does not exceed 18 mg/kg. 1,3-Dichloropropene also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 1,3-dichloropropene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with 1,3-dichloropropene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by 1,3-dichloropropene and may provide protection for periods greater than 8 hours: polyvinyl alcohol and Viton (fluorocarbon rubber). A material that may withstand permeation for more than 4 but fewer than 8 hours is Teflon (polytetrafluoroethylene). Butyl rubber, natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by 1,3-dichloropropene.

If 1,3-dichloropropene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 1,3-dichloropropene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 1,3-dichloropropene. Contact lenses should not be worn when working with this material.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2,2-DICHLOROPROPIONIC ACID

INTRODUCTION

This guideline summarizes pertinent information about 2,2-dichloropropionic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_4Cl_2O_2$

- **Structure**

$H_3C{-}CCl_2{-}COOH$

- **Synonyms**

Alatex; Basfapon; BH Dalapon; Basinex; Crisapon; Dalapon; Dalapon 85; Ded-Weed; Devipon; a-dichloropropionic acid; Dowpon; Dowpon M; Gramevin; Kenapon; Liropon; Proprop; Radapon; Revenge; Unipon

- **Identifiers**

1. CAS No.: 75-99-0
2. RTECS No.: UF0690000
3. DOT UN: 1760 60
4. DOT label: Corrosive

- **Appearance and odor**

2,2-Dichloropropionic acid is a corrosive, colorless liquid with an acrid odor. The commercial herbicide is a white or tan powder from the sodium and/or magnesium salt. The odor threshold for 2,2-dichloropropionic acid is reported to be 2,500 mg/m^3 (416 ppm).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 142.97
2. Boiling point (760 mm Hg): 185° to 190°C (365° to 374°F)
3. Specific gravity (water = 1): 1.4 at 20°C (68°F)
4. Vapor density: 4.93
5. Melting point: 174° to 176°C (345.2° to 348.8°F)
6. Vapor pressure: 10 mm Hg at 40°C (104°F)
7. Solubility: Very soluble in water, alcohol, and ether.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame.

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 2,2-dichloropropionic acid.

4. Special precautions: 2,2-Dichloropropionic acid is corrosive to iron, aluminum, and copper.

- **Flammability**

The National Fire Protection Association has not issued a fire hazard rating for 2,2-dichloropropionic acid; this substance is not flammable but may burn.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, regular foam, or carbon dioxide to fight fires involving 2,2-dichloropropionic acid. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving 2,2-dichloropropionic acid should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Containers of 2,2-dichloropropionic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2,2-dichloropropionic acid. Structural firefighters' protective clothing may provide limited protection against fires involving 2,2-dichloropropionic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 2,2-dichloropropionic acid [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (6 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for 2,2-dichloropropionic acid [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2,2-dichloropropionic acid a threshold limit value (TLV) of 1 ppm (5.8 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of skin, eye, respiratory, and gastrointestinal irritation associated with 2,2-dichloropropionic acid exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2,2-dichloropropionic acid can occur through inhalation, ingestion, and eye or skin contact; absorption through the skin is said to be "negligible."

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to 2,2-dichloropropionic acid in liquid or vapor form causes corrosion of the eyes and skin; chronic exposure may cause kidney injury. Applied to the skin of rabbits, the sodium salt of 2,2-dichloropropionic acid caused necrosis, and instillation of this substance into the eyes of rabbits caused reversible conjunctival irritation [ACGIH 1991]. The oral LD_{50} in rats is >5,000 mg/kg [NIOSH 1994]. The oral LD_{50} in rats for sodium 2,2-dichloropropionic acid is 9,330 mg/kg (male) and 7,570 mg/kg (female) [Farm Chemicals Handbook 1994]. Exposure to an atmosphere saturated with 2,2-dichloropropionic acid for 7 hours produced no observable effects in rats [ACGIH 1991]. Rats fed 15 mg/kg/day of this substance for 120 days had no ill effects [ACGIH 1991]. Dogs fed 100 mg/kg/day of 2,2-dichloropropionic acid for 1 year and rats given 50 mg/kg/day for the same period showed increased

kidney weights at autopsy [ACGIH 1991]. Dogs given 50 mg/kg/day for 1 year or rats given 15 mg/kg/day for 2 years, showed no significant changes at autopsy [ACGIH 1991].

2. *Effects on Humans:* Exposure to 2,2-dichloropropionic acid causes irritation of the eyes, respiratory tract, and skin, and contact of the eyes or skin with the liquid or vapor can lead to burns. Repeated or prolonged skin contact may cause dermatitis [NJDH 1989]. Exposure to a 2- to 7 ppm concentration of this substance for an unspecified time produced respiratory irritation described as "minimal" [ACGIH 1991], and systemic poisoning caused by acute exposure to an unspecified concentration of this substance resulted in lassitude, vomiting, diarrhea, slowed pulse, and anorexia [NLM 1994].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 2,2-dichloropropionic acid include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, sneezing, difficulty breathing, and reddened and cracked skin. Lassitude, anorexia, vomiting, and diarrhea have also been reported. In contact with the eyes or skin, the vapor or liquid of this substance may cause eye or skin burns.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged skin exposure to 2,2-dichloropropionic acid include reddened, cracked, and blistered skin. Long-term high exposure to 2,2-dichloropropionic acid may affect the liver and kidneys.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Immediately initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2,2-dichloropropionic acid! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2,2-dichloropropionic acid or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve 2,2-dichloropropionic acid and lead to worker exposures to this substance:

—Use as a herbicide

The following methods are effective in controlling worker exposures to 2,2-dichloropropionic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2,2-dichloropropionic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, skin, liver, and kidneys. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society (ATS) [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2,2-dichloropropionic acid at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or findings consistent with diseases of the respiratory system, skin, liver, or kidneys.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2,2-dichloropropionic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2,2-dichloropropionic acid on the respiratory system, skin, liver, or kidneys. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2,2-dichloropropionic acid.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 2,2-dichloropropionic acid is made using a silica gel tube (150/75 mg sections; 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with deionized water to extract the 2,2-dichloropropionic acid. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1993].

PERSONAL HYGIENE

2,2-Dichloropropionic acid is corrosive; therefore, if this substance contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with 2,2-dichloropropionic acid should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of 2,2-dichloropropionic acid, particularly its potential to cause burns of the skin on contact.

A worker who handles 2,2-dichloropropionic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2,2-dichloropropionic acid or a solution containing 2,2-dichloropropionic acid is handled, processed, or stored.

STORAGE

2,2-Dichloropropionic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of 2,2-dichloropropionic acid should be protected from physical damage and should be stored separately from aluminum and ferric compounds. Because containers that formerly contained 2,2-dichloropropionic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2,2-dichloropropionic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the 2,2-dichloropropionic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  2,2-Dichloropropionic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for 2,2-dichloropropionic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 2,2-dichloropropionic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although 2,2-dichloropropionic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2,2-dichloropropionic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with 2,2-dichloropropionic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2,2-dichloropropionic acid permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2,2-dichloropropionic acid.

If 2,2-dichloropropionic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2,2-dichloropropionic acid might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2,2-dichloropropionic acid. Contact lenses should not be worn if the potential exists for 2,2-dichloropropionic acid exposure.

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Occupational Health Guideline for Dichlorotetrafluoroethane (Refrigerant 114)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $F_2ClCCClF_2$
- Synonyms: 1,2-Dichlorotetrafluoroethane; Freon 114; Refrigerant 114; Halon 242
- Appearance and odor: Colorless liquid or gas with a very slight ethereal odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Refrigerant 114 is 1000 parts of Refrigerant 114 per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7000 milligrams of Refrigerant 114 per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Refrigerant 114 can affect the body if it is inhaled or if the liquid comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Breathing in very high concentrations may cause drowsiness and unconsciousness and may also cause the heart to beat irregularly or to stop suddenly. If the liquid gets on the skin or in the eyes, it may cause frostbite.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Refrigerant 114.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Refrigerant 114 at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from Refrigerant 114 exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Refrigerant 114 might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of Refrigerant 114 might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Refrigerant 114 vapor is a respiratory irritant and causes asphyxia at extremely high concentrations. Exposure to 200,000 ppm for 16 hours was fatal to dogs, while single 8-hour exposures produced tremors and convulsions but no fatalities; repeated exposures at 140,000 to 160,000 ppm for 8 hours caused incoordination, tremors, and occasionally convulsions, but all dogs survived. At 47,000 ppm guinea pigs developed respiratory irritation. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest, probably due to sensitization of the myocardium. The liquid spilled on the skin may produce frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 170.9
  2. Boiling point (760 mm Hg): 3.5 C (38.4 F)

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3. Specific gravity (water = 1): 1.44
4. Vapor density (air = 1 at boiling point of Refrigerant 114): 5.9
5. Melting point: −94 C (−137 F)
6. Vapor pressure at 20 C (68 F): 1444 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.01
8. Evaporation rate (butyl acetate = 1): Higher than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Refrigerant 114 reacts with chemically active metals such as sodium. potassium, calcium, powdered aluminum, zinc, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when Refrigerant 114 decomposes.
4. Special precautions: Liquid Refrigerant 114 will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Although Refrigerant 114 has a chloroform-like odor, no quantitative data are available relating warning properties to air concentrations. It is treated, therefore, as a material with poor warning properties.
Refrigerant 114 is not a known eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for Refrigerant 114 is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming wet with liquid Refrigerant 114.
- Any clothing which becomes wet with liquid Refrigerant 114 should be removed immediately and not reworn until the Refrigerant 114 has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid Refrigerant 114 may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Refrigerant 114 may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and use in aerosols with other Freons to lower vapor pressure and produce non-flammable aerosol propellants; use as a refrigerant in industrial cooling and airconditioning systems	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a blowing agent for cellular polymers; use as a solvent and diluent in polymerization of fluoro-olefins, cleaning and degreasing printed circuit boards, preparation of explosives, and extraction of volatile substances	General dilution ventilation; local exhaust ventilation; personal protective equipment

Use as a foaming agent in fire extinguishing and aerosols; in organic synthesis in preparation of uranium tetrafluoride, Freons, and polymer intermediates	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in inhibiting of metal erosion in hydraulic fluids; in strengthening glass bottles; in magnesium refining; and as a reflux liquid to assist heat removal	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid Refrigerant 114 gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid Refrigerant 114 gets on the skin, immediately flush the contaminated skin with water if the Refrigerant 114 has not already evaporated. If liquid Refrigerant 114 soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of Refrigerant 114, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When Refrigerant 114 has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Refrigerant 114 is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow.
3. If the liquid is spilled or leaked, allow to vaporize.

REFERENCES

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RESPIRATORY PROTECTION FOR REFRIGERANT 114

Condition	**Minimum Respiratory Protection*** **Required Above 1000 ppm**
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dichlorvos

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3O)_2POOCH=CCl_2$ or $C_4H_7Cl_2O_4P$
- Synonyms: DDVP; 2,2-dichlorovinyl dimethyl phosphate
- Appearance and odor: Colorless to amber liquid with a mild chemical odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dichlorvos is 1 milligram of dichlorvos per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dichlorvos can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of dichlorvos, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing dichlorvos, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to all the above symptoms, weakness, generalized twitching, and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heart beat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to dichlorvos may make a person more susceptible to the effects of this and related chemicals. Repeated exposure to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dichlorvos.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dichlorvos at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Cholinesterase determination: Dichlorvos (DDVP) causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to any new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determi-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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nation which should be performed quarterly or at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Dichlorvos (DDVP) is an anticholinesterase agent; absorption may occur from inhalation of the vapor or mist, from skin absorption of the liquid, or from ingestion. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscle, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms may occur promptly or may be delayed for up to 12 hours. After inhalation, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects, such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for weeks after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects. In a study of 13 workers exposed for 12 months to an average concentration of 0.7 mg/m^3, the erythrocyte cholinesterase activity was reduced by approximately 35%, and the serum cholinesterase activity was reduced by 60%; the results of other tests and of thorough medical examinations conducted at regular intervals were entirely normal.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 221
2. Boiling point (1 mm Hg): 77 C (170 F)
3. Specific gravity (water = 1): 1.44
4. Vapor density (air = 1 at boiling point of dichlorvos): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 32 C (90 F): 0.032 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1 (approx).
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride gas, phosphoric acid mist, and carbon monoxide) may be released in a fire involving dichlorvos.
4. Special precautions: Dichlorvos will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dichlorvos.
2. Eye Irritation Level: Dichlorvos is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of dichlorvos, it is treated as a material with poor warning properties. The concentration in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for dichlorvos is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with dichlorvos.
- Clothing contaminated with dichlorvos should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dichlorvos from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dichlorvos, the person performing the operation should be informed of dichlorvos's hazardous properties.
- Non-impervious clothing which becomes contaminated with dichlorvos should be removed immediately and not reworn until the dichlorvos is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dichlorvos may contact the eyes.

SANITATION

- Skin that becomes contaminated with dichlorvos should be immediately washed or showered with soap or mild detergent and water to remove any dichlorvos.
- Employees who handle dichlorvos should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dichlorvos may occur and control methods which may be effective in each case:

Operation	Controls
Formulation and mixing for insecticidal application	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Application on vegetables, animals, agriculutral premises, and for outdoor fogging; insecticidal use of tablets, rubbing devices, resin strips, animal collars, dust on animals, animal buildings, restaurants, hospitals, and aircraft	Personal protective equipment
Manufacture of dichlorvos	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dichlorvos or dichlorvos mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dichlorvos or dichlorvos mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dichlorvos or dichlorvos mists soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of dichlorvos, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dichlorvos has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Under-

stand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dichlorvos is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Dichlorvos may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR DICHLORVOS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate or Vapor Concentration	
10 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 200 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dichlorvos; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICROTOPHOS

INTRODUCTION

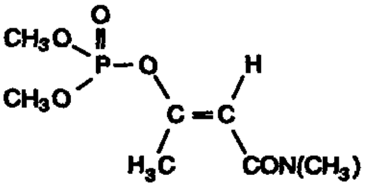
This guideline summarizes pertinent information about dicrotophos for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8H_{16}NO_5P$

- **Structure**



- **Synonyms**

Bidrin; phosphoric acid, dimethyl ester; ester with (E)-3-hydroxy-N,N-dimethylcrotonamide; Bidirl; Carbicron; Ektafos; Oleobidrin; 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl phosphate (E)-isomer; dimethyl 1-dimethylcarbonyl-1-propen-2-yl phosphate

- **Identifiers**

1. CAS No.: 141-66-2
2. RTECS No.: TC3850000
3. DOT NA: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Dicrotophos is a yellow-brown liquid with a mild ester odor. Eighty-five percent of the commercial grade consists of the E-isomer, which is amber in color and more insecticidally active than the Z-isomer.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 237.21
2. Boiling point (760 mm Hg): 400°C (752°F)
3. Specific gravity (water = 1): 1.22 at 15°C (59°F)
4. Vapor density: Data not available
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.0001 mm Hg
7. Solubility: Miscible with water, methylene chloride, ethanol, isopropyl and diacetone alcohols, acetoni-

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trile, and xylene; slightly soluble in kerosene and diesel fuel.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: None reported.
3. Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen) may be released in a fire involving dicrotophos.
4. Special precautions: Dicrotophos is somewhat corrosive to cast iron, mild steel, brass, and stainless steel 304.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to dicrotophos.

1. Flash point: Greater than 93°C (200°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving dicrotophos.

Fires involving dicrotophos should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of dicrotophos may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicrotophos. Chemical protective clothing that is specifically recommended for dicrotophos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving dicrotophos.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicrotophos [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.25 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for dicrotophos. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicrotophos a threshold limit value (TLV) of 0.25 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to dicrotophos [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to dicrotophos.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicrotophos can occur through inhalation, ingestion, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Dicrotophos is a highly toxic organophosphorus pesticide that causes cholinesterase inhibition in animals [EPA 1989]. The dermal LD$_{50}$ in rabbits is 168 mg/kg [NIOSH 1993]. The 4-hr LC$_{50}$ in rats is 90 mg/m^3 [NIOSH 1993]. The oral LD$_{50}$ is 13 mg/kg in rats and 11 mg/kg in mice [NIOSH 1993]. Rats fed dicrotophos for 2 years at a dietary level of 1, 10, or 100 ppm showed no effects at the 1-ppm level

but had decreased body weights and reduced cholinesterase activity at the higher levels [ACGIH 1991]. Dogs fed 0.16, 1.6, or 16 ppm for 2 years experienced mild episodes of excessive salivation and, at the highest dose, showed depressed plasma and red blood cell cholinesterase activity [ACGIH 1991].

2. *Effects on Humans:* Dicrotophos is an inhibitor of plasma and red blood cell cholinesterase activity in humans. There are two reports of severe poisoning attributed to dicrotophos, one involving a 41-year-old farmer who had applied this substance to his crops and used it inside his house to control insects, and the other involving a 52-year-old man who ingested a mixture of turpentine and dicrotophos after a drinking bout [Hayes 1982]. Both of these patients eventually recovered after initially responding to treatment and then relapsing seriously [Hayes 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dicrotophos include those of cholinesterase inhibition: headache, nausea, dizziness, anxiety, restlessness, muscle twitching, weakness, tremor, incoordination, vomiting, abdominal cramps, and diarrhea; excessive salivation, sweating, tearing of the eyes, and runny nose also may occur.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to dicrotophos include persistent anorexia, weakness, and malaise, brought on by repeated absorption of dicrotophos in amounts that are not sufficient to cause acute poisoning.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** rinse concentrated solutions, vapors, mists, or aerosols of dicrotophos from the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dicrotophos. Dicrotophos can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If vapors, mists, or aerosols of dicrotophos are inhaled, move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicrotophos or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicrotophos and lead to worker exposures to this substance:

—Manufacture, formulation, and application of dicrotophos-containing insecticides and acaricides to cotton, apples, grains, vegetables, ornamentals, shrubs, trees, and other crops

The following methods that are effective in controlling worker exposures to dicrotophos, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dicrotophos, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A pre-exposure red blood cell and plasma cholinesterase activity baseline should also be established.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dicrotophos at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma or red blood cell cholinesterase activity.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicrotophos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicrotophos on red blood cell and plasma cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophorus compounds such as dicrotophos. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for dicrotophos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70 percent of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because a patient who has recovered from the acute phase of organophosphorus poisoning remains hypersusceptible to anticholinesterases for as long as several weeks or months, the need for medical monitoring may extend well beyond the acute poisoning episode.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicrotophos is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. The sample is then treated with toluene to extract the dicrotophos. Analysis is conducted by gas chromatography using a flame photometric detector. This method is included in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

Dicrotophos can be absorbed through the skin in toxic amounts. Therefore, if dicrotophos contacts the skin, workers should immediately and repeatedly wash the body (including hair, scalp, and nails) with soap and water. Get medical help immediately.

Clothing contaminated with dicrotophos should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicrotophos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles dicrotophos should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicrotophos or a solution containing dicrotophos is handled, processed, or stored.

STORAGE

Dicrotophos should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must be located at a suitable distance from inhabited buildings, animal shelters, and food stores and must be inaccessible to unauthorized persons. Containers of dicrotophos should be protected from physical damage, heat, sparks, and open flame. Dicrotophos decomposes when stored at temperatures about 25°C to 30°C (77°F to 86°F). Containers should be stacked in a manner that permits free circulation of air at the bottom and insides of the stacks of containers.

SPILLS AND LEAKS

In the event of a spill or leak involving dicrotophos, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Use water spray to reduce vapors; do not get water inside the container.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the dicrotophos for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 100 lb or more of dicrotophos must comply with EPA's emergency planning requirements [40 CFR 355.40].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for dicrotophos is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the State emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicrotophos emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicrotophos is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicrotophos exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, full-body covering, and head protection) should be worn as appropriate to prevent any possibility of skin contact with dicrotophos. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicrotophos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have shown that material made of a laminate of Vitron/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. Since specific test data are not available for dicrotophos, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicrotophos.

If dicrotophos is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicrotophos might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dicrotophos.

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CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

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NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICYCLOPENTADIENE

INTRODUCTION

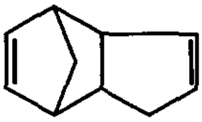
This guideline summarizes pertinent information about dicyclopentadiene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{12}$

- **Structure**



- **Synonyms**

1,3-Cyclopentadiene, dimer; alpha-dicyclopentadiene (endo form); bicyclopentadiene; biscyclopentadiene; cyclopentadiene dimer; 3a,4,7,7a-tetrahydro-4,7-methanoindene

- **Identifiers**

1. CAS No.: 77-73-6
2. RTECS No.: PC1050000
3. DOT UN: 2048 26
4. DOT label: Flammable liquid (or solid)

- **Appearance and odor**

Dicyclopentadiene is a flammable tricyclic compound that exists either as a solid or a clear liquid, depending on temperature. In the solid state, dicyclopentadiene is a colorless, combustible crystalline substance that has a disagreeable camphor-like odor. Dicyclopentadiene exists in two stereoisomeric forms, the endo and exo isomers; the commercial product consists predominantly of the endo isomer. The odor is detectable below 0.2 ppm, but does not become noticeably irritating below 10 ppm.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 132.21
2. Boiling point (760 mm Hg): 172°C (342°F); depolymerizes at boiling point to form two molecules of cyclopentadiene.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Specific gravity (water = 1): 0.98 at 35°C (95°F)

4. Vapor density (air = 1 at boiling point of dicyclopentadiene): 4.6

5. Melting point: 32°C (89.6°F)

6. Vapor pressure at 20°C (68°F): 1.4 mm Hg

7. Solubility: Insoluble in water; soluble in acetic acid and alcohol; very soluble in ether and carbon tetrachloride.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of dicyclopentadiene with oxidizing agents can cause fires and explosions.

3. Hazardous decomposition products: Thermal-oxidative degradation products can include cyclopentadiene and partial oxidation products of carbon monoxide and carbon dioxide. When heated to decomposition, dicyclopentadiene emits acrid smoke and fumes.

4. Special precautions: Dicyclopentadiene must be inhibited and maintained under an inert atmosphere to prevent hazardous polymerization. In contact with air, especially when heated, dicyclopentadiene forms peroxides; the level of these can be controlled by the addition of an inhibitor.

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to dicyclopentadiene.

1. Flash point: 32°C (90°F) (open cup)

2. Autoignition temperature: 503°C (937°F)

3. Flammable limits in air: Lower, 0.8; upper, 6.3

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol-resistant foam, or water fog to fight fires involving dicyclopentadiene.

Fires involving dicyclopentadiene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of dicyclopentadiene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadiene. Structural firefighters' protective clothing may provide limited protection against fires involving dicyclopentadiene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicyclopentadiene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (30 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for dicyclopentadiene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicyclopentadiene a threshold limit value (TLV) of 5 ppm (27 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation associated with dicyclopentadiene exposure. The ACGIH limit is based on the risk of irritation, kidney damage, and pulmonary effects associated with exposure to dicyclopentadiene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicyclopentadiene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dicyclopentadiene is an irritant of the eyes and skin and a narcotic on acute exposure; chronic exposure causes kidney and lung damage. Applied to the skin of rabbits, dicyclopentadiene causes moderate to severe irritation; instilled into the rabbit eye, this substance causes mild and reversible irritation [NIOSH 1993; Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 5,080 mg/kg [NIOSH 1993]. The 4-hr LC_{50} is 145 ppm in mice and 372 ppm in rats [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50} is 353 mg/kg in rats and 190 mg/kg in mice [NIOSH 1993]. Acutely poisoned animals showed signs of eye irritation, lost coordination, and convulsed before death [ACGIH 1991]. Rats exposed daily for 10 days to dicyclopentadiene concentrations of 72 or 146 ppm survived, but rats exposed on the same regimen to a concentration of 332 ppm died [ACGIH 1991]. Rats exposed to a 35- or 74-ppm concentration of dicyclopentadiene for 7 hours/day for 89 days showed, at autopsy, kidney damage and some lung involvement [ACGIH 1991]. Leukocytosis was found in rats 96-hr post-subcutaneous administration of dicyclopentadiene [Clayton and Clayton 1981; NLM 1992].

2. *Effects on Humans:* Dicyclopentadiene is an irritant of the eyes, nose, throat, and skin in humans [NJDH 1989]. Exposed workers also experience headaches and other central nervous system effects [NLM 1992]. Workers exposed accidentally to a high but unspecified concentration of dicyclopentadiene experienced headaches for the first two months after exposure but did not continue to experience this symptom indicating a certain degree of inurement [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dicyclopentadiene include redness, tearing, and inflammation of the eyes, sneezing, and coughing. Contact of the skin with this substance causes redness and may cause blistering. Headaches and loss of coordination also may occur after an acute overexposure.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dicyclopentadiene may include those associated with kidney damage, such as blood, pus, or protein in the urine, or with lung damage, such as difficult breathing, rales, and fluid in the lungs.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dicyclopentadiene. ***Immediately and thoroughly*** flush eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicyclopentadiene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicyclopentadiene and lead to worker exposures to this substance:

—Use as a chemical intermediate during chlorinated hydrocarbon pesticide synthesis and to stabilize organophosphorus insecticides

—Use in the production of ferrocene and other metallocene compounds

—Use as an intermediate in the production of plasticizers, elastomers, pharmaceuticals, resins, paints, varnishes, paint driers, and perfumes

—Use as a polyhalogenated flame retardant for plastics

The following methods are effective in controlling worker exposures to dicyclopentadiene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dicyclopentadiene, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dicyclopentadiene at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, kidneys, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicyclopentadiene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadiene on the eyes, skin, kidneys, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dicyclopentadiene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicyclopentadiene is made using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the dicyclopentadiene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is abstracted in the *OSHA Chemical Information Manual* [OSHA 1987] and can be found in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If dicyclopentadiene contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dicyclopentadiene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicyclopentadiene, particularly its potential to cause skin irritation.

A worker who handles dicyclopentadiene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicyclopentadiene or a solution containing dicyclopentadiene is handled, processed, or stored.

STORAGE

Dicyclopentadiene should be stored in a cool, dry, well-ventilated area in tightly sealed, stainless steel containers that are maintained under an inert blanket and are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet requirements for an OSHA Class IB flammable liquid. Only explosion-proof ventilation may be used. Containers of dicyclopentadiene should be protected from physical damage and should be stored separately from oxidizing materials, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dicyclopentadiene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dicyclopentadiene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. Use non-sparking tools for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
8. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
9. For large liquid spills, build dikes far ahead of the spill to contain the dicyclopentadiene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) regulatory requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dicyclopentadiene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dicyclopentadiene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicyclopentadiene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicyclopentadiene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicyclopentadiene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with dicyclopentadiene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicyclopentadiene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicyclopentadiene.

If dicyclopentadiene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicyclopentadiene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dicyclopentadiene. Contact lenses should not be worn if the potential exists for dicyclopentadiene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICYCLOPENTADIENYL IRON

INTRODUCTION

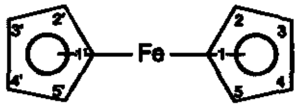
This guideline summarizes pertinent information about dicyclopentadienyl iron for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$(C_5H_5)_2Fe$

- **Structure**



- **Synonyms**

Ferrotsen; ferrocene; biscyclopentadienyl iron; di-2,4-cyclopentadien-1-yl iron; iron bis(cyclopentadiene); iron bis(cyclopentadienide); iron dicyclopentadienyl; bis(eta(5)-2,4-cyclopentadien-1-yl)-iron

- **Identifiers**

1. CAS No.: 102-54-5
2. RTECS No.: LK0700000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Dicyclopentadienyl iron is a flammable, bright orange, crystalline solid with a camphor-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 186.05
2. Boiling point (760 mm Hg): 249°C (408.2°F) (sublimes above 100°C (212°F))
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: 173°-174°C (343°-345°F)
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water; soluble in alcohol, ether, and benzene
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, open flame, and steam
2. Incompatibilities: Contact of dicyclopentadienyl iron

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

with tetranitromethane may lead to violent explosions. This substance also reacts violently with ammonium perchlorate and mercury (II) nitrate.

3. Hazardous decomposition products: Thermal oxidative decomposition of dicyclopentadienyl iron can produce acrid smoke and irritating fumes.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to dicyclopentadienyl iron. Other sources rate dicyclopentadienyl iron as a moderate fire risk.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: No information is available on the proper extinguishant for fires involving dicyclopentadienyl iron.

Fires involving dicyclopentadienyl iron should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of dicyclopentadienyl iron may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadienyl iron.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for dicyclopentadienyl iron is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicyclopentadienyl iron a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and NIOSH limits are based on the risk of mutagenicity associated with exposure to dicyclopentadienyl iron [54 Fed. Reg. 2592; NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicyclopentadienyl iron can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to dicyclopentadienyl iron may cause liver, red blood cell, and testicular changes in experimental animals. The LC_{50} for an unspecified period of time in rats is greater than 150 mg/m^3 [Hathaway et al. 1991]. The oral LD_{50} is 1,320 mg/kg in rats and 832 mg/kg in mice [NIOSH 1993]. Ten 200 mg/kg oral doses of dicyclopentadienyl iron administered over a 2-week period caused no fatalities in rats [Hathaway et al. 1991]. In a 6-month subchronic study in dogs, oral doses of 30 to 300 mg/kg/day dicyclopentadienyl iron caused hemosiderosis (iron deposits) in the liver [Hathaway et al. 1991; ACGIH 1991]. Dogs exposed to a 300-mg/kg/day dose of dicyclopentadienyl iron for an unspecified period of time developed cirrhosis of the liver; reversible decreases in hemoglobin, packed red cell volume, and red cell count were also seen in these animals within the first 4 weeks of exposure on this regimen [Hathaway et al. 1991]. Testicular hypoplasia developed in dogs given oral dicyclopentadienyl iron doses of 100 mg/kg/day for 6 months [Hathaway et al. 1991; ACGIH 1991]. Dicyclopentadienyl iron is mutagenic in mouse lymphoma test systems [NLM 1992].

2. *Effects on Humans:* No data are available on the

effects of exposure to dicyclopentadienyl iron in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to dicyclopentadienyl iron have been reported in humans.
2. *Chronic exposure:* Based on effects seen in animals, chronic exposure to dicyclopentadienyl iron may cause liver, red blood cell, or testicular damage.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicyclopentadienyl iron or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicyclopentadienyl iron and lead to worker exposures to this substance:

—Use as an additive in oil and gasoline fuel to improve efficiency of combustion and eliminate smoke

—Manufacture of rubber, silicone resins, and high-temperature polymers

—Use as coating for missiles and satellites

—Use as a combustion catalyst

The following methods are effective in controlling worker exposures to dicyclopentadienyl iron, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dicyclopentadienyl iron, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood and liver.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dicyclopentadienyl iron at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the blood or liver.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicyclopentadienyl iron exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadienyl iron on the blood or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dicyclopentadienyl iron.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicyclopentadienyl iron is made using a mixed cellulose ester filter (MCEF) with a 0.8-micron pore size. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy (or by inductively coupled argon plasma atomic emission spectroscopy). This method has a sampling and analytical error of 0.16 and is described in OSHA Methods No. ID-121 and No. ID-125G in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If dicyclopentadienyl iron contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with dicyclopentadienyl iron should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicyclopentadienyl iron.

A worker who handles dicyclopentadienyl iron should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicyclopentadienyl iron is handled, processed, or stored.

STORAGE

Dicyclopentadienyl iron should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of dicyclopentadienyl iron should be protected from physical damage and should be stored separately from ammonium perchlorate, tetranitromethane, mercury (II) nitrate, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dicyclopentadienyl iron may still hold product residues, they should be handled appropriately.

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In the event of a spill or leak involving dicyclopentadienyl iron, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, take up with activated carbon or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the dicyclopentadienyl iron for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dicyclopentadienyl iron is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dicyclopentadienyl iron; there is no reportable quantity for this substance.

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  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicyclopentadienyl iron emitted or released from their facility annually.

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EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicyclopentadienyl iron is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicyclopentadienyl iron exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as necessary) should be worn to prevent skin contact with dicyclopentadienyl iron. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicyclopentadienyl iron permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicyclopentadienyl iron.

If dicyclopentadienyl iron is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicyclopentadienyl iron might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dicyclopentadienyl iron. Contact lenses should not be worn if the potential exists for dicyclopentadienyl iron exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIELDRIN

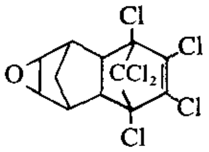
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about dieldrin for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_8Cl_6O$
- **Structure:**



- **Synonyms:** Dieldrex; dieldrine; 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro,endo,exo-1,4:5,8-dimethanonaphthalene; illoxol; octalox
- **Identifiers:** CAS 60-57-1; RTECS IO1750000; DOT 2761
- **Appearance and odor:** Light brown crystals with a mild chemical odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 380.90
2. Boiling point (at 760 mmHg): Decomposes
3. Specific gravity (water = 1): 1.75
4. Vapor density (air = 1 at boiling point of dieldrin): 13.2
5. Melting point: 176°C (349°F)
6. Vapor pressure at 20°C (68°F): 1.8×10^{-7} mmHg
7. Solubility in water, mg/l water at 25°-29°C (77°-84°F): 0.186

- **Reactivity**

1. Incompatibilities: Dieldrin may react with concentrated mineral acids, acid catalysts, acid oxidizing agents, phenols, or reactive metals.
2. Hazardous decomposition products: Hydrochloric acid fumes and other chlorinated decomposition products may be released in a fire involving dieldrin.
3. Caution: Dieldrin should be stored in a tightly closed container in a well-ventilated area.

- **Flammability**

Nonflammable

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for dieldrin is 0.25 milligrams of dieldrin per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that dieldrin be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limt. The NIOSH recommended exposure limit (REL) is 0.15 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.25 mg/m^3 (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for dieldrin

	Exposure limits mg/m^3
OSHA PEL TWA (Skin)*	0.25
NIOSH REL TWA (Ca)†	0.15§
ACGIH TLV® (Skin)	0.25

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ Lowest reliably detectable level.

NOTE: Most uses of dieldrin were suspended by the Environmental Protection Agency, effective October 18, 1974. The only

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uses allowed are direct soil application, seed treatment if labeled "not for food use," dipping of plant roots and tops, subsurface termite control, and hot-caps.

HEALTH HAZARD

- **Routes of exposure**

Dieldrin may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact. Dermal absorption is substantially increased when dieldrin is dissolved in organic solvents.

- **Summary of toxicology**

1. *Effects on animals:* Acute oral administration of dieldrin to rats caused liver and kidney degeneration. Chronic oral administration of dieldrin produced enlarged livers and increased liver enzyme activities in mice and rats, liver and lung cancers in mice, and adrenal cancer in rats. Dieldrin fed to pregnant mice and hamsters caused increased fetal deaths, congenital anomalies, and growth retardation in the offspring.
2. *Effects on humans:* Dieldrin is a neurotoxin and may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to dieldrin can cause hyperirritability, headache, dizziness, nausea, vomiting, blood in the urine, tremors, convulsions, and coma.
2. *Long-term (chronic):* Exposure to dieldrin can cause dermatitis, weight loss, muscular twitching, and convulsions.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to dieldrin, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic or laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, liver, kidneys, and hematopoietic (blood-cell-forming), reproductive, and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to dieldrin at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include: preexisting chronic diseases of the skin, liver, kidneys, and hematopoietic and reproductive systems. Workers should inform their physicians of their potential for exposures to dieldrin because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter." The physician should obtain baseline values for liver function tests and a complete blood count with a reticulocyte count.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to dieldrin. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and hematopoietic, reproductive, and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to dieldrin may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Non-autoimmune hemolytic anemia.
2. Delayed onset SHE's include: Cataract, toxic hepatitis, and non-autoimmune hemolytic anemia.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to dieldrin should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting dieldrin with glass fiber filters followed by extraction with isooctane and analysis by gas chromatography. A detailed sampling and analytical method for dieldrin may be found in the *NIOSH Manual of Analytical Methods* (method number S283).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with dieldrin.

SANITATION

Clothing which is contaminated with dieldrin should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of dieldrin from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of dieldrin's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with dieldrin should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle dieldrin should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to dieldrin may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for dieldrin

Operations	Controls
During formulation and handling of insecticide	Personal protective equipment, local exhaust ventilation
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to dieldrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

If dieldrin gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to dieldrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If dieldrin gets on the skin, wash it immediately with soap and water. If dieldrin penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If dieldrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Dieldrin solid may be collected and placed in an appropriate container.
3. Dieldrin dust may be collected by vacuuming with an appropriate high-efficiency filtration system.
4. For small quantities of liquids containing dieldrin, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing dieldrin may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for dieldrin

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHANOLAMINE

INTRODUCTION

This guideline summarizes pertinent information about diethanolamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{11}NO_2$

- **Structure**

$HO(CH_2)_2NH(CH_2)_2OH$

- **Synonyms**

N,N-Diethanolamine; iminodiethanol; diolamine; diethylolamine; 2,2'-dihydroxydiethylamine; DEA; bis(2-hydroxyethyl)amine; 2,2'iminobisethanol

- **Identifiers**

1. CAS No.: 111-42-2
2. RTECS No.: KL2975000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Diethanolamine is a combustible substance that can exist in the form of colorless crystals or a viscous liquid at room temperature. It has a mild, ammonia-like odor and is usually found in liquid form.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 105.14
2. Boiling point (760 mm Hg): 269°C (516.2°F) (decomposes)
3. Specific gravity (water = 1): 1.09 at 30°C (86°F)
4. Vapor density (air = 1 at boiling point of diethanolamine): 3.65
5. Melting point: 28°C (82.4°F)
6. Vapor pressure at 20°C (68°F): Less than or equal to 0.01 mm Hg
7. Solubility: Very soluble in water and alcohol; insoluble in ether and benzene; miscible with acetone and methanol.

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8. Evaporation rate (ether = 1): Greater than 5,000

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. Diethanolamine reacts with carbon dioxide in the air.

2. Incompatibilities: Contact of diethanolamine with oxidizing agents or acidic materials can cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide, carbon dioxide, and oxides of nitrogen) may be released in a fire involving diethanolamine.

4. Special precautions: Diethanolamine is corrosive to copper, copper alloys, zinc, and galvanized iron.

Flammability

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethanolamine.

1. Flash point: 138°C (280°F) (open cup)

2. Autoignition temperature: 661.5°C (1,224°F)

3. Flammable limits in air (% by volume): Lower, 1.6; upper, 9.8

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol foam, or water spray. A solid stream of water or foam directed into burning liquid diethanolamine may cause frothing. Use water spray to cool fire-exposed containers and to dilute liquid to a less flammable solution.

Fires involving diethanolamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethanolamine.

XPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diethanolamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 3 ppm (15 mg/m^3) as a TWA for up to 10-hr workday and a 40-hr workweek for diethanolamine [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethanolamine a threshold limit value (TLV) of 3 ppm (13 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of eye and skin irritation associated with exposure to diethanolamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethanolamine can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Diethanolamine is an irritant of the eyes and skin and, when administered orally or intraperitoneally, a kidney and liver toxin in animals. Applied to rabbit skin in a 10-percent solution, diethanolamine caused redness, and the application of more concentrated solutions caused a greater degree of injury [Clayton and Clayton 1981]. Instillation of the undiluted liquid or a 40-percent solution into rabbit eyes caused severe burns; whereas, 15 percent solution produces only minor damage [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 12.2 g/kg [NIOSH 1993]. The oral LD_{50} is 710 mg/kg in rats, 3,300 mg/kg in mice, and 2,200 mg/kg in rabbits [NIOSH 1993]. Animals given large intraperitoneal doses lose the righting reflex, become uncoordinated and cyanotic, and die [Gosselin et al. 1984]. Rats administered 100 or 500 mg/kg

diethanolamine intraperitoneally were autopsied 4 or 24 hours after dosing and showed cytoplasmic vacuolization of the liver and kidneys and, at the higher dose, renal tubular degeneration [Hathaway et al. 1991]. At autopsy, rats fed 0.17 g/kg for 90 days showed cloudy swelling and degeneration of kidney tubules and fatty degeneration of the liver [Hathaway et al. 1991].

2. *Effects on Humans:* Diethanolamine causes irritation of the eyes, nose, and throat in humans, and contact of the skin with this substance can cause minor burns of the skin. Splashed into the eye, diethanolamine may cause severe burns [NJDH 1989].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethanolamine may include redness, inflammation, and tearing of the eyes; inflamed eyelids; coughing; and sneezing. Splashed into the eye, this substance may cause severe eye burns, with corneal necrosis and permanent damage.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged skin contact with diethanolamine include dryness and cracking of the skin and minor burns.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of diethanolamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diethanolamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diethanolamine and lead to worker exposures to this substance:

—Use as a liquid detergent in cleaners, polishes, textile specialties, paints, cutting oils, and shampoos

—Use as an absorbent for acid gases

—Use as an emulsifier and dispersing agent in various agricultural chemicals, cosmetics, and pharmaceuticals

—Manufacture of rubber chemicals, surface-active ingredients, and petroleum demulsifiers

—Use as a chemical intermediate in the manufacture of resins and plasticizers

—Use as a humectant and softening agent, in the production of lubricants for the textile industry, and in organic syntheses

The following methods are effective in controlling worker exposures to diethanolamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to diethanolamine, the licensed health care professioanl should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diethanolamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethanolamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethanolamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diethanolamine.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diethanolamine is made using a coated XAD-2 tube (80/40 mg sections, 20/60 mesh); the coating is 10 percent 1-naphthylisothiocyanate (NITC). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with dimethylformamide to extract the diethanolamine derivative. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If diethanolamine contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with diethanolamine should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of diethanolamine, particularly its potential to cause skin irritation.

A worker who handles diethanolamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diethanolamine or a solution containing diethanolamine is handled, processed, or stored.

STORAGE

Diethanolamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diethanolamine should be protected from physical damage and should be stored separately from oxidizers, acidic materials, heat, sparks, and open flame. Because containers that formerly contained diethanolamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethanolamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Mix with inert absorbent materials such as dry sand or vermiculite and place in appropriate containers for disposal.

6. Flush these residues with large quantities of water after neutralizing with sodium bisulfate.

7. Do not flush to sewers or open waterways.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diethanolamine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR Part 355.40] to notify the National Response Center of an accidental release of diethanolamine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 lb more or otherwise use 10,000 lb or more of diethanolamine per calendar year are required by EPA [40 CFR Part 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethanolamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diethanolamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diethanolamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged skin contact with diethanolamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by diethanolamine and may provide protection for periods greater than 8 hours: butyl rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton®.

If diethanolamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diethanolamine might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diethanolamine. Contact lenses should not be worn if the potential exists for diethanolamine exposure.

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Occupational Health Guideline for Diethylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5)_2NH$
- Synonyms: None
- Appearance and odor: Colorless liquid with a fishy odor, like ammonia.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diethylamine is 25 parts of diethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 75 milligrams of diethylamine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for diethylamine a Threshold Limit Value of 3 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diethylamine can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Diethylamine vapors may cause irritation of the respiratory tract, causing coughing, chest pain, or immediate or delayed breathing difficulties. High vapor concentrations may also cause severe irritation of the eyes. Contact of the liquid with bare skin may cause irritation. Covered contact as with clothing wet with diethylamine may cause skin burns. Contact of the liquid with the eyes is an emergency and may result in serious eye injury.

2. Long-term Exposure: Prolonged or repeated skin contact with liquid diethylamine may cause chronic irritation. Prolonged or repeated contact of the eyes with vapors of diethylamine at levels near the irritant level often results in swelling of the eye, causing foggy vision and the appearance of halos around lights.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diethylamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from diethylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of diethylamine might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Diethylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Diethylamine is a severe eye irritant and may cause tissue damage. Persons with pre-existing eye problems may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Diethylamine vapor is a severe irritant to mucous membranes, eyes, and skin. Rabbits repeatedly exposed to 50 ppm for 7 hours daily showed corneal damage and pulmonary irritation. In one reported human case, liquid splashed into the eye caused immediate intense pain. In spite of emergency irrigation and treatment the cornea became swollen and cloudy. Some permanent

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visual impairment resulted. Contact with the liquid causes vesiculation and necrosis of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

1. Molecular weight: 73.14
2. Boiling point (760 mm Hg): 55.5 C (132 F)
3. Specific gravity (water = 1): 0.71
4. Vapor density (air = 1 at boiling point of diethylamine): 2.5
5. Melting point: −50 C (−58 F)
6. Vapor pressure at 20 C (68 F): 195 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 16.9

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving diethylamine.
4. Special precautions: Liquid diethylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −18 C (less than 0 F) (closed cup)
2. Autoignition temperature: 312 C (594 F)
3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 10.1
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The MCA's *Material Safety Data Sheet* states that "diethylamine has a strong ammoniacal odor which gives good warning of its presence." The Department of Transportation's CHRIS manual for the Coast Guard gives an odor threshold of 0.14 ppm.
2. Eye Irritation Level: Grant reports that "chronic exposure to the vapors at concentrations as low as 50 ppm in air causes conjunctival and pulmonary irritation in rabbits; corneal erosion develops after 2 weeks of exposure." Patty notes that both edema of the cornea and eye irritation have been observed during industrial exposures to diethylamine. The concentrations producing these effects are not given. Permanent eye injury is reported to occur after repeated exposure to 50 ppm, according to Brieger and Hodes.
3. Other Information: The MCA's *Material Safety Data Sheet* states that diethylamine is a respiratory tract irritant, and the AIHA *Hygienic Guide* reports that this compound irritates mucous membranes. No quantitative information is given.
4. Evaluation of Warning Properties: Since the odor threshold of diethylamine (0.14 ppm) is well below the permissible exposure limit, this substance is considered to have good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors in a silica gel tube, followed by desorption with sulfuric acid in methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure diethylamine may be used. An analytical method for diethylamine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid diethylamine, where skin contact may occur.
- Clothing wet with liquid diethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diethylamine from the clothing. If the clothing is to be

laundered or otherwise cleaned to remove the diethylamine, the person performing the operation should be informed of diethylamine's hazardous properties.

- Where exposure of an employee's body to liquid diethylamine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with or non-impervious clothing which becomes contaminated with liquid diethylamine should be removed immediately and not reworn until the diethylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid diethylamine or solutions containing more than 0.5 percent by weight of diethylamine contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where solutions containing 0.5 percent or less of diethylamine by weight may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid diethylamine or solutions containing more than 0.5 percent by weight of diethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid diethylamine should be immediately washed or showered to remove any diethylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of textile finishing agents, surfactants, rubber processing chemicals, agricultural chemicals, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a corrosion inhibitor in iron, steel, and metal industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as polymerization inhibitor and catalyst in polymer industry; intermediate in dye industry	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as depilatory of animal skins; and in electroplating solutions	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If diethylamine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If diethylamine gets on the skin, immediately flush the contaminated skin with water. If diethylamine soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of diethylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When diethylamine has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If diethylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely

clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Diethylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of diethylamine vapors are permitted.

- Waste disposal method:

Diethylamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DIETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
1250 ppm or less	A chemical cartridge respirator with a full facepiece and an cartridge(s) which provide protection against diethylamine. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against diethylamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against diethylamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Diethylamino Ethanol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5)_2NC_2H_4OH$
- Synonyms: 2-Diethylaminoethyl alcohol; N,N-diethylethanolamine; diethyl (2-hydroxytriethyl) amine; 2-diethylamino ethanol; 2-hydroxy-triethylamine
- Appearance and odor: Colorless liquid with a weak ammonia odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diethylamino ethanol is 10 parts of diethylamino ethanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 50 milligrams of diethylamino ethanol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diethylamino ethanol can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Liquid diethylamino ethanol splashes will cause skin irritation. Liquid splashes in the eye will cause irritation and damage. Diethylamino ethanol vapor may cause nausea and vomiting. It may also cause cough and shortness of breath. Splashes may cause eye and skin irritation.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diethylamino ethanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diethylamino ethanol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from diethylamino ethanol exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of diethylamino ethanol might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Diethylamino ethanol is a primary skin irritant and a probable skin sensitizer. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Diethylamino ethanol is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Diethylamino ethanol vapor is a skin, eye, and respiratory irritant. Rats exposed to 500 ppm 6 hours daily for 5 days exhibited marked eye and nasal irritation, and a number of animals had corneal opacity by the end of the third day; the mortality rate was 20%, and at autopsy there was acute purulent bronchiolitis and bronchopneumonia. Daily exposure at 200 ppm for up to 6 months was fatal in some rats, with death occurring during the first 30 days. An attempt by a laboratory worker to remove animals from an inhalation chamber containing approximately 100 ppm resulted in nausea and vomiting within 5 minutes after a brief exposure; no irritation of the eyes or throat was noted during this

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brief exposure. Other persons in the same room also complained of a nauseating odor but showed no ill effects. The liquid is a severe skin irritant; in the guinea pig it is a skin sensitizer. It is also a severe eye irritant and may produce permanent eye injury. No systemic effects from human exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 117.2
  2. Boiling point (760 mm Hg): 162 C (324 F)
  3. Specific gravity (water = 1): 0.89
  4. Vapor density (air = 1 at boiling point of diethylamino ethanol): 4.0
  5. Melting point: Data not available
  6. Vapor pressure at 20 C (68 F): 1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
  8. Evaporation rate (butyl acetate = 1): 0.17
- **Reactivity**
  1. Conditions contributing to instability: Heat.
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause spattering.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving diethylamino ethanol.
  4. Special precautions: Liquid diethylamino ethanol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 52 C (126 F) (closed cup)
  2. Autoignition temperature: 320 C (608 F)
  3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 11.7
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: Diethylamino ethanol has a weak ammoniacal odor, but no information is available concerning its odor threshold.
  2. Eye Irritation Level: The Pennwalt Corporation *Material Safety Data Sheet* states that diethylamino ethanol is irritating to the eyes. Deichmann and Gerarde (in *Toxicology of Drugs and Chemicals*, p. 216) state that 2-diethylamino ethanol as the "undiluted" compound is a severe eye irritant capable of producing permanent eye injury. No information is available, however, concerning air concentrations producing eye irritation.
  3. Other Information: Deichmann and Gerarde report that the vapors of diethylamino ethanol irritate the respiratory tract, but the concentrations producing this irritation are not given.
  4. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of diethylamino ethanol to air concentrations, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for diethylamino ethanol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid diethylamino ethanol, where skin contact may occur.
- Clothing contaminated with liquid diethylamino ethanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diethylamino ethanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diethylamino ethanol, the person performing the operation should be informed of diethylamino ethanol's hazardous properties.
- Where exposure of an employee's body to liquid diethylamino ethanol may occur, facilities for quick

drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with liquid diethylamino ethanol should be removed immediately and not reworn until the diethylamino ethanol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of solutions containing 5 percent or more of diethylamino ethanol by weight contacting the eyes and where solutions containing less than 5 percent diethylamino ethanol by weight may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to solutions containing 5 percent or more of diethylamino ethanol by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid diethylamino ethanol should be immediately washed or showered to remove any diethylamino ethanol.
- Employees who handle liquid diethylamino ethanol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diethylamino ethanol may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of medicinals and pharmaceuticals, pesticides, protective surface coatings for metals, emulsifying agents for polishes, resinous materials for treating fiber surfaces, fluorescent brightening agents, and in polymer production	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis to prepare compounds for surfactants, detergents, wetting agents, and yarn-treating	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthetic fiber dyeing and vat dyes; use as photographic stabilizing solutions	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If diethylamino ethanol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If diethylamino ethanol gets on the skin, immediately flush the contaminated skin with water. If diethylamino ethanol soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of diethylamino ethanol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When diethylamino ethanol has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If diethylamino ethanol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Diethylamino ethanol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explo-

sion. Sewers designed to preclude the formation of explosive concentrations of diethylamino ethanol vapors are permitted.

- Waste disposal methods:

Diethylamino ethanol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Diethylamino Ethanol*, New York, 1974.

RESPIRATORY PROTECTION FOR DIETHYLAMINO ETHANOL

Condition	**Minimum Respiratory Protection*** **Required Above 10 ppm**
Vapor Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of diethylamino ethanol; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHYLENETRIAMINE

INTRODUCTION

This guideline summarizes pertinent information about diethylenetriamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{13}N_3$

- **Structure**

$(NH_2CH_2CH_2)_2NH$

- **Synonyms**

DETA; N-(2-aminoethyl)1,2-ethanediamine; 2,2'-diaminodiethylamine; aminoethylethandiamine; bis(2-aminoethyl)amine; bis(beta-aminoethyl)amine; N,N-bis(2-aminoethyl)amine; 2,2'-iminobisethylamine

- **Identifiers**

1. CAS No.: 111-40-0
2. RTECS No.: IE1225000
3. DOT UN: 2079 29
4. DOT label: Corrosive

- **Appearance and odor**

Diethylenetriamine is a combustible, somewhat viscous, colorless to yellow liquid with an ammonia-like odor. This substance is hygroscopic and strongly alkaline.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 103.17
2. Boiling point (760 mm Hg): 207°C (405°F)
3. Specific gravity (water = 1): 0.96 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of diethylenetriamine): 3.56
5. Melting point: -39°C (-38°F)
6. Vapor pressure at 20°C (68°F): 0.37 mm Hg
7. Solubility: Completely soluble in water; soluble in hydrocarbons; insoluble in ether.
8. Evaporation rate (ether = 1): Greater than 400

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Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of diethylenetriamine with oxidizing materials or strong acids may cause a violent reaction; in contact with cellulose nitrate, this substance ignites spontaneously. In contact with silver, cobalt, or chromium compounds, certain diethylenetriamine complexes can be explosive.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon, and hydrocarbons) may be released in a fire involving diethylenetriamine.

4. Special precautions: Diethylenetriamine is corrosive to copper and its alloys.

Flammability

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethylenetriamine.

1. Flash point: 98°C (208°F) (open cup)

2. Autoignition temperature: 358°C (676°F)

3. Flammable limits in air (percent by volume): Lower, 2; upper, 6.7

4. Extinguishant: Use water spray, alcohol foam, carbon dioxide, or dry chemical to fight fires involving diethylenetriamine. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving diethylenetriamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of diethylenetriamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if there is discoloration of a container due to fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethylenetriamine. Structural firefighters' protective clothing may provide limited protection against fires involving diethylenetriamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) had not promulgated a permissible exposure limit (PEL) for diethylenetriamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for diethylenetriamine of 1 ppm (4 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek with a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethylenetriamine a threshold limit value (TLV) of 1 ppm (4.2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned diethylenetriamine a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of skin and respiratory tract irritation and sensitization associated with exposure to diethylenetriamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethylenetriamine can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Diethylenetriamine is a severe irritant of the eyes and skin in animals. Application of this substance to rabbit skin caused severe injury, and instillation into the eyes of rabbits caused maximum damage to the cornea [Clayton and Clayton 1981; Grant 1986]. The dermal LD_{50} in rabbits is 1,090 mg/kg [NIOSH 1994]. Acutely poisoned animals convulsed and exhibited signs of gastrointestinal irritation before death [NIOSH 1994]. Rats exposed once to a 300-ppm concentration of diethylenetriamine for 8 hours survived [ACGIH 1986]. The oral LD_{50} in rats is 1,080 mg/kg [NIOSH 1994].

2. *Effects on Humans:* Diethylenetriamine is a severe irritant of the eyes, skin, mucous membranes, and upper respiratory tract and a potent skin and pulmonary sensitizer in humans. In contact with the skin, diethylenetriamine causes severe irritation, with edema and sometimes necrosis [Grant 1986]. A majority of workers chronically exposed to this substance are reported to develop sensitization to it. Exposure to the heated vapor of diethylenetriamine (concentration not specified) causes respiratory tract irritation, and pulmonary sensitization is reported to occur with "relatively high frequency" [NLM 1993; ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethylenetriamine vapors include eye and respiratory tract irritation, with tearing and redness of the eyes, coughing, and difficult breathing. Contact of the eyes or skin with the liquid causes corneal or skin burns, with blistering, swelling, redness, and cell death.

2. *Chronic exposure*: Repeated exposure to diethylenetriamine may cause an asthmatic response in sensitized individuals. Repeated contact of the skin with this substance may cause dermatitis, with redness and scaling, or skin sensitization, accompanied by redness, itching, and the development of wheals.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of diethylenetriamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diethylenetriamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diethylenetriamine and lead to worker exposures to this substance:

—Use as a solvent for sulfur, acid gases, and various resins and dyes

—Use as a saponification agent for acidic materials and as a fuel component

—Use as an intermediate in the manufacture of pharmaceuticals

The following methods are effective in controlling worker exposures to diethylenetriamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to diethylenetriamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diethylenetriamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of pulmonary or skin allergies and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethylenetriamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethylenetriamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diethylenetriamine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diethylenetriamine is made using a coated XAD-2 tube (80/40 mg sections, 20/60 mesh); the coating is 10 percent (w/w) 1-naphthylisothiocyanate (NITC). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with dimethylformamide to extract the diethylenetriamine. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Analytical Methods Manual* as OSHA Method No. 60 [OSHA 1985].

PERSONAL HYGIENE

If diethylenetriamine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then by wash with soap and water.

Clothing contaminated with diethylenetriamine should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of diethylenetriamine, particularly its potential to cause burns of the eyes and skin.

A worker who handles diethylenetriamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, applying cosmetics, or using toilet facilities.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diethylenetriamine or a solution containing diethylenetriamine is handled, processed, or stored.

STORAGE

Diethylenetriamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage should be in low-fire-risk areas, out of direct sunlight. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of diethylenetriamine should be protected from physical damage and should be stored separately from acids, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained diethylenetriamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethylenetriamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the diethylenetriamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous quantities, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diethylenetriamine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of diethylenetriamine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethylenetriamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diethylenetriamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diethylenetriamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with diethylenetriamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by diethylenetriamine and may provide protection for periods greater than 8 hours: butyl rubber, neoprene, and Viton . Natural rubber, nitrile rubber, polyvinyl alcohol, and polyvinyl chloride are not recommended.

If diethylenetriamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diethylenetriamine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diethylenetriamine. Contact lenses should not be worn if the potential exists for diethylenetriamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHYL PHTHALATE

INTRODUCTION

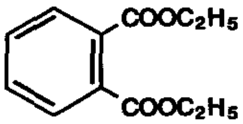
This guideline summarizes pertinent information about diethyl phthalate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_4(COOC_2H_5)_2$

- **Structure**



- **Synonyms**

1,2-Benzenedicarboxylic acid diethyl ester; Anozol; DEP; diethyl o-phthalate; Estol 1550; ethyl phthalate; Neantine; Palatinol A; phthalic acid, diethyl ester; Phthalol; Placidol E; Solvanol; Unimoll DA.

- **Identifiers**

1. CAS No.: 84-66-2
2. RTECS No.: TI1050000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Diethyl phthalate is a flammable, clear, colorless, oily liquid with a bitter, disagreeable taste and a slight ester odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.24
2. Boiling point (760 mm Hg): 298°C (568.4°F)
3. Specific gravity (water = 1): 1.12 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of diethyl phthalate): 7.66
5. Melting point: -40.5°C (-40°F)
6. Vapor pressure at 163°C (325°F): 14 mm Hg
7. Solubility: Insoluble in water; miscible with alcohols,

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

ketones, esters, and aromatic hydrocarbons; partly miscible with aliphatic solvents.

8. Evaporation rate (ether = 1): Greater than 300

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Contact of diethyl phthalate with strong acids, strong oxidizing agents, nitric acid, permanganates, or water causes a violent reaction.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, carbon dioxide, and various hydrocarbons) may be released in a fire involving diethyl phthalate.
4. Special precautions: Diethyl phthalate attacks some forms of plastic.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethyl phthalate.

1. Flash point: 163°C (325°F) (open cup)
2. Autoignition temperature: 457°C (855°F)
3. Flammable limits in air (percent by volume): Lower, 0.7 (@368°F); upper, data not available
4. Extinguishant: Use dry chemical, water spray, alcohol foam, or carbon dioxide to fight fires involving diethyl phthalate. Water spray and foam are effective but may cause frothing. Water may be used to cool fire-exposed containers.

Fires involving diethyl phthalate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Cool containers from the sides with water until well after the fire is out. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethyl phthalate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diethyl phthalate [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethyl phthalate a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on mild toxic effects and smaller than normal fetuses in animals associated with diethyl phthalate exposure; the ACGIH limit is based on the risks of polyneuritis and vestibular dysfunction associated with exposure to diethyl phthalate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethyl phthalate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to diethyl phthalate causes irritation of the eyes, mucous membranes, and skin and may have reproductive effects in animals. Applied to the skin of rats, 50% of a 30- to 40-mg/kg dose of diethyl phthalate was excreted unchanged within 1 week, and the unexcreted dose remained in the area of application [Hathaway et al. 1991]. Instilled into rabbit eyes, diethyl phthalate caused mild irritation. Guinea pigs exposed to a 511-ppm concentration of diethyl phthalate for 6 hr showed signs of mild skin irritation, and cats exposed to a 10-mg/L concentration of this substance for 5 hr showed signs of nasal irritation [Clayton and Clayton 1981]. The oral LD$_{50}$ is 8,600 mg/kg in rats and 6,172 mg/kg in mice [NIOSH 1993]. Male rats and mice given diethyl phthalate by oral administration developed testicular and other reproductive effects [NIOSH 1993; HSDB 1992]. Diethyl phthalate is mutagenic in bacterial test systems [NIOSH 1993].

2. *Effects on Humans:* Diethyl phthalate has irritant effects on the eyes, mucous membranes, and skin of humans and also causes central nervous system effects in exposed workers. Exposure to the heated vapors of diethyl phthalate is reported to have caused transient nose and throat irritation [ACGIH 1991]. In a study of Russian workers exposed to several phthalates (butyl phthalate, higher alkyl phthalates, dioctyl phthalate, diisooctyl phthalate, and benzyl butyl phthalate) at average ambient concentrations of 1.7 to 66 mg/m^3, 32% of workers were found to have signs and symptoms of polyneuritis; 78% of those workers who reported experiencing adverse effects also showed signs of vestibular dysfunction. The toxic effects seen in these workers were related to the duration of exposure and occurred only after 6 or 7 years of exposure to this group of phthalates [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethyl phthalate include redness and inflammation of eyes and eyelids, runny nose, scratchy throat, headache, dizziness, and nausea.

2. *Chronic exposure:* Chronic exposure to diethyl phthalate may cause signs and symptoms associated with polyneuritis and vestibular dysfunction, including pain, numbness, weakness, and spasms in the arms and legs, dizziness, and nausea.

- **Emergency procedures**

> WARNING!
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from concentrated solutions, vapors, mists, or aerosols of diethyl phthalate. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of diethyl phthalate is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diethyl phthalate and lead to worker exposures to this substance:

—Use as a solvent for cellulose acetate in the manufacture of varnishes and dopes

—Use as an alcohol denaturant

—Use as a mosquito repellant, plasticizer in solid rocket propellants, wetting agent, and camphor substitute

—Use as a fixative and solvent in perfumes

The following methods are effective in controlling worker exposures to diethyl phthalate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the period of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to diethyl phthalate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diethyl phthalate at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethyl phthalate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethyl phthalate on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diethyl phthalate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diethyl phthalate is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) and a glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. The sample is then treated with carbon disulfide to extract the diethyl phthalate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Chemical Information System [OSHA 1990].

PERSONAL HYGIENE

If diethyl phthalate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, followed by washing with soap and water.

Clothing contaminated with diethyl phthalate should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of diethyl phthalate, particularly its potential to be irritating to the skin and eyes.

A worker who handles diethyl phthalate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diethyl phthalate or a solution containing diethyl phthalate is handled, processed, or stored.

STORAGE

Diethyl phthalate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diethyl phthalate should be protected from physical damage and should be stored separately from acids, bases, strong oxidizing agents, moisture, heat, sparks, and open flame. Because containers that formerly contained diethyl phthalate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethyl phthalate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.

2. Ventilate the area of the spill or leak.

3. Take up small spills with paper or other absorbent material for disposal.

4. Build a dike far ahead of the spill area to contain the spill for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diethyl phthalate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for diethyl phthalate is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hour period, in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of diethyl phthalate per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethyl phthalate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Diethyl phthalate is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U088. It is approved for land disposal as long as the concentration of diethyl phthalate in the waste or treatment residual does not exceed 28-mg/kg. Diethyl phthalate also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diethyl phthalate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard 29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent prolonged or repeated skin contact with diethyl phthalate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. 4H (PE/EVAL) has been recommended for use against permeation by diethyl phthalate and may provide protection for more than 4 but fewer than 8 hr. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diethyl phthalate.

If diethyl phthalate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diethyl phthalate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and washing facilities should be available within the immediate work area whenever the potential exists for eye or skin contact with diethyl phthalate. Contact lenses should not be worn if the potential exists for diethyl phthalate exposure.

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Occupational Health Guideline for Difluorodibromomethane (Freon 12B2)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CBr_2F_2
- Synonyms: Dibromodifluoromethane; Freon 12B2
- Appearance and odor: Colorless liquid or gas with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Freon 12B2 is 100 parts of Freon 12B2 per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 860 milligrams of Freon 12B2 per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Freon 12B2 can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to Freon 12B2 may cause irritation of the nose and throat, drowsiness, unconsciousness, and death. Exposure may also cause liver damage. If the liquid gets on the skin or in the eyes, it may cause frostbite.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Freon 12B2.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Freon 12B2 at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from Freon 12B2 exposure.

—Liver disease: Although Freon 12B2 is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Freon 12B2 might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Freon 12B2 vapor is a respiratory irritant and a narcotic. Rats exposed to 4000 ppm for 15 minutes showed pulmonary edema, while 2300 ppm daily for 6 weeks resulted in the death of more than half the animals. At 2300 ppm dogs showed rapid and progressive signs of intoxication, with weakness and loss of balance after a few days' exposure, followed by convulsions. These dogs at autopsy had pulmonary congestion, centrolobular necrosis of the liver, and some evidence of central nervous system damage. However, other dogs tolerated daily exposures of 350 ppm for 7 months without signs of intoxication. No systemic effects have been reported from industrial exposures. In liquid form, this substance may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 209.8

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

2. Boiling point (760 mm Hg): 24.5 C (76.1 F)

3. Specific gravity (water = 1): 2.46

4. Vapor density (air = 1 at boiling point of Freon 12B2): 7.2

5. Melting point: −141.6 C (−223 F)

6. Vapor pressure at 20 C (68 F): 620 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Higher than 1

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Freon 12B2 reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide and hydrogen fluoride) may be released when Freon 12B2 decomposes.

4. Special precautions: Liquid Freon 12B2 will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Freon 12B2 does not have adequate warning properties. Freon 12B2 is not a known eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of Freon 12B2 vapors using an adsorption tube with subsequent desorption with isopropyl alcohol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure Freon 12B2 may be used. An analytical method for Freon 12B2 is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid Freon 12B2.
- Non-impervious clothing which becomes wet with liquid Freon 12B2 should be removed promptly and not reworn until the Freon 12B2 has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid Freon 12B2 may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Freon 12B2 may occur and control methods which may be effective in each case:

Operation	Controls
Use as a fire extinguishing agent; use in organic synthesis	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in processing cutting tools as razor blades, hypodermic needles, scalpels, culinary knives, and garden tools	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a special solvent for preparation of explosive mixtures	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid Freon 12B2 gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid Freon 12B2 gets on the skin, immediately flush the contaminated skin with water if the liquid Freon 12B2 has not already evaporated. If liquid Freon 12B2 soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of Freon 12B2, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When Freon 12B2 has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Freon 12B2 is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow.
3. If the liquid is spilled or leaked, allow to vaporize.

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RESPIRATORY PROTECTION FOR FREON 12B2

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
DIGLYCIDYL ETHER
POTENTIAL HUMAN CARCINOGEN

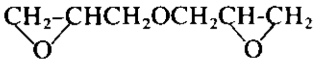
INTRODUCTION

This guideline summarizes pertinent information about diglycidyl ether (DGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{10}O_3$

- **Structure:**



$\mathrm{CH_2{-}CHCH_2OCH_2CH{-}CH_2}$ (O O)

- **Synonyms:** Bis(2,3-epoxypropyl) ether; DGE; di(2,3--epoxypropyl) ether; di(2,3-epoxy)propyl ether

- **Identifiers:** CAS 2238-07-05; RTECS KN2350000; DOT not assigned

- **Appearance and odor:** Colorless liquid with a strong, irritating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.16
2. Boiling point (at 760 mmHg): 260°C (500°F)
3. Specific gravity (water = 1): 1.26
4. Vapor density (air = 1 at boiling point of DGE): 4.49
5. Vapor pressure at 25°C (77°F): 0.09 mmHg
6. Saturation concentration in air (approximate) at 25°C (77°F): 0.0121% (121 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Ethers as a class tend to form peroxides upon contact with air and exposure to light.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving DGE.
3. Caution: DGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 64°C (147°F)
2. Extinguishant: Dry chemical, carbon dioxide, alcohol foam
3. Class IIIA Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

1. Odor threshold: Approximately 5 ppm
2. Eye irritation levels: 10 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DGE is 0.5 parts of DGE per million parts of air (ppm) [2.8 milligrams of DGE per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded. The National Institute for Occupational Safety and Health (NIOSH) recommends that DGE be controlled and handled as a potential human carcinogen in the workplace and that exposure be reduced to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.2 ppm (1 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.1 ppm (0.5 mg/m^3) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for diglycidyl ether

	Exposure limits	
	ppm	mg/m³
OSHA PEL Ceiling	0.5	2.8
NIOSH REL (Ca)*		
Ceiling (15 min)	0.2	1
ACGIH TLV® TWA	0.1	0.5

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

DGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: In mice and rats, acute inhalation or oral administration of DGE caused central nervous system depression, incoordination, breathing difficulty (dyspnea), respiratory failure, and death. In rats and rabbits, acute or subchronic inhalation or dermal administration of DGE produced weight loss, corneal opacities, testicular degeneration, and abnormalities of the blood-forming tissues including lymphoid atrophy of the thymus and depression of white blood cell and bone marrow cell counts. In skin-painting studies, DGE produced tumors in mice. DGE was mutagenic in bacterial test systems.

• Signs and Symptoms of exposure

1. *Short-term (acute):* Exposure to DGE can cause skin burns and severe irritation of the skin, eyes, and respiratory tract.
2. *Long-term (chronic):* Exposure to DGE can cause dermatitis and skin sensitization.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to DGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, reproductive, respiratory, nervous, and hematopoietic (blood cell forming) systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DGE at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, reproductive, nervous, respiratory and hematopoietic systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DGE may cause adverse reproductive effects or diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of DGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting DGE vapors with charcoal adsorption tubes followed by desorption with methylene chloride and analysis by gas chromatography. Refer to the *Criteria for Recommended Standard. . . . Occupational Exposure to Glycidyl Ethers* for limitations and correct use of this method. Direct-reading devices calibrated to measure DGE may also be used if available.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with DGE.

SANITATION

Clothing which is contaminated with DGE should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DGE's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with DGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

DGE is not generally used outside of research laboratories. There are no common industrial uses for DGE.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to DGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DGE gets on the skin, wash it immediately with soap and water. If DGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities of liquids containing DGE, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing DGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing DGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for diglycidyl ether

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type or self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

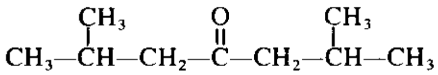
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIISOBUTYL KETONE

INTRODUCTION

This guideline summarizes pertinent information about diisobutyl ketone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_9H_{18}O$
- **Structure:**



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

- **Synonyms:** DBK; diisopropyl acetone; 2,6-dimethyl-4-heptanone; isovalerone; valerone
- **Identifiers:** CAS 108-83-8; RTECS MJ5775000; DOT 1157, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a mild ketone odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 142.27
2. Boiling point (at 760 mmHg): 169.4°C (336.9°F)
3. Specific gravity (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of diisobutyl ketone): 4.9
5. Melting point: -46°C (-51°F)
6. Vapor pressure: At 20°C (68°F), 1.7 mm Hg; at 25°C (77°F), 2.4 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.05
8. Evaporation rate (butyl acetate = 1): 0.17
9. Saturation concentration in air (approximate): At 20°C (68°F), 0.22% (2,200 ppm); at 25°C (77°F), 0.32% (3,200 ppm)

- **Reactivity**

1. Incompatabilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving diisobutyl ketone.
3. Caution: Diisobutyl ketone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 60°C (140°F) (closed cup)
2. Autoignition temperature: 396°C (745°F)
3. Flammable limits in air, % by volume at 100°C: Lower, 0.8; upper, 7.1
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.11 ppm
2. Eye irritation level: 25 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, diisobutyl ketone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, diisobutyl ketone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for diisobutyl ketone is 50 parts of diisobutyl ketone per million parts of air (ppm) [290 milligrams of diisobutyl ketone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 25 ppm (140 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 25 ppm (150 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Table 1.—Occupational exposure limits for diisobutyl ketone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	50	290
NIOSH REL TWA	25	140
ACGIH TLV® TWA	25	150

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diisobutyl ketone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute inhalation or oral administration of diisobutyl ketone by rats or guinea pigs caused drowsiness, impaired muscular coordination (ataxia), damage to the lungs, liver, or kidneys, and death.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to diisobutyl ketone can cause headache, dizziness, drowsiness, tearing, and irritation of the eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to diisobutyl ketone can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to diisobutyl ketone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to diisobutyl ketone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to diisobutyl ketone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to diisobutyl ketone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting diisobutyl ketone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure diisobutyl ketone may also be used if available. A detailed sampling and analytical method for diisobutyl ketone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with diisobutyl ketone.

Workers should be provided with and required to use splash-proof safety goggles where diisobutyl ketone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with diisobutyl ketone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of diisobutyl ketone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of diisobutyl ketone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with diisobutyl ketone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle diisobutyl ketone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to diisobutyl ketone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for diisobutyl ketone

Operations	Controls
During use as a paint thinner; during use as a solvent in the production of synthetic coatings, soap, or nitrocellulose	General dilution ventilation, local exhaust ventilation, personal protective equipment
During use as an intermediate in organic synthesis, an extractant in the pharmaceutical industry, a separating agent in the chemical industry, or a dispersant in the manufacture of resins	General dilution ventilation, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to diisobutyl ketone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If diisobutyl ketone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to diisobutyl ketone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If diisobutyl ketone gets on the skin, wash it immediately with soap and water. If diisobutyl ketone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If diisobutyl ketone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing diisobutyl ketone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from diisobutyl ketone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing diisobutyl ketone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Diisobutyl ketone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing diisobutyl ketone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for diisobutyl ketone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 625 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 1,250 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 2,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 2,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 25 ppm (140 mg/m^3) (TWA).

Occupational Health Guideline for Diisopropylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2CH\text{-}NH\text{-}CH(CH_3)_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with an odor like ammonia.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diisopropylamine is 5 parts of diisopropylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 20 milligrams of diisopropylamine per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diisopropylamine can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Diisopropylamine may cause headache, visual problems and nausea. It may also cause irritation of the respiratory tract.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diisopropylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diisopropylamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from diisopropylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of diisopropylamine might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Diisopropylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Diisopropylamine is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Diisopropylamine vapor is a respiratory irritant and a severe eye irritant. Exposure of experimental animals to 260 to 2200 ppm for several hours resulted in fatalities at the higher concentrations as a result of severe pulmonary damage; exposure at these concentrations for several hours caused clouding of the cornea which was reversible. Workers exposed to concentrations between 25 and 50 ppm complained of nausea, headache, and disturbances in vision. Diisopropylamine has been reported to cause skin irritation in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 101.2
  2. Boiling point (760 mm Hg): 84 C (183 F)
  3. Specific gravity (water = 1): 0.72

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4. Vapor density (air = 1 at boiling point of diisopropylamine): 3.5

5. Melting point: −96 C (−141 F)

6. Vapor pressure at 20 C (68 F): 60 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions below 27 C (81 F). Above this temperature, the maximum solubility is 30%.

8. Evaporation rate (butyl acetate = 1): 5.8

- **Reactivity**

1. Conditions contributing to instability: Heat.

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause spattering.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving diisopropylamine.

4. Special precautions: Liquid diisopropylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −6.7 C (20 F) (closed cup)

2. Autoignition temperature: 316 C (600 F)

3. Flammable limits in air, % by volume: Lower: 0.8; Upper: 7.1

4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Diisopropylamine has an odor like ammonia, but no quantitative information is available concerning its odor threshold.

2. Eye Irritation Level: Grant reports that visual disturbances have been observed in men who have been exposed to concentrations of 25 to 50 ppm diisopropylamine. "Experimental exposures of rabbits, guinea pigs, rats, and cats have established that the vapor is injurious to the corneal epithelium." According to Grant, "this is presumably the cause of the visual disturbances observed in men." A several-hour exposure to concentrations of 260 to 2200 ppm has caused corneal injury to experimental animals.

3. Other Information: The *Documentation of TLV's* reports that Treon et al. observed irritation of the respiratory mucous membranes in animals exposed repeatedly to 260 ppm.

4. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of diisopropylamine, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for diisopropylamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid diisopropylamine.
- Clothing wet with liquid diisopropylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diisopropylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diisopropylamine, the person performing the operation should be informed of diisopropylamine's hazardous properties.
- Any clothing which becomes wet with liquid diisopropylamine should be removed immediately and not reworn until the diisopropylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of solutions containing 5 percent or more of diisopropylamine by weight contacting the eyes and where solutions containing less than 5 percent of diisopropylamine by weight may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to solutions containing 5 percent or more of diisopropylamine by weight, an eye-wash foun-

tain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid diisopropylamine should be promptly washed or showered to remove any diisopropylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diisopropylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of corrosion inhibitors in iron and steel	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthesis of herbicides, delayed action vulcanization accelerator for sulfur-cured rubbers; as a catalyst for chemical synthesis of alkylene cyanohydrin	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as component in gels for cosmetic and medical applications as deodorants and aftershave solutions	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If diisopropylamine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If diisopropylamine gets on the skin, immediately wash the contaminated skin with water. If diisopropylamine soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of diisopropylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When diisopropylamine has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If diisopropylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Diisopropylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of diisopropylamine vapors are permitted.

- Waste disposal method:

Diisopropylamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DIISOPROPYLAMINE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dimethyl Acetamide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CON(CH_3)_2$
- Synonyms: N,N-dimethyl acetamide; DMAC
- Appearance and odor: Colorless liquid with a faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethyl acetamide is 10 parts of dimethyl acetamide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of dimethyl acetamide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethyl acetamide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Repeated or prolonged exposure to dimethyl acetamide may cause liver damage with yellow jaundice. Repeated exposure at high concentrations may cause depression, drowsiness, confusion, and hallucinations.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethyl acetamide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethyl acetamide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver should be stressed.

—Liver function tests: Since liver damage has been observed in humans exposed to dimethyl acetamide, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Inhalation of the vapor or skin absorption of the liquid causes liver damage. Repeated dermal application of the liquid to dogs at a dosage level of 4.0 ml/kg for 6 weeks caused severe fatty infiltration of the liver. Repeated exposure of rats to a concentration of 195 ppm for 6 months resulted in focal necrosis of the liver; exposure to 40 ppm for the same period of time caused no adverse effects. Workers repeatedly exposed to 20 to 25 ppm developed jaundice; appreciable skin absorption was thought to have occurred. Dimethyl acetamide has a significant antitumor effect in animals. Nine patients with neoplastic disease were given daily doses of 400 mg/kg by an unspecified route for 3 or more days as a therapeutic trial; they experienced depression, lethargy, confusion, and disorientation; on the last (4th or 5th) day of therapy or within 24 hours thereafter, the patients had visual and auditory hallucinations, perceptual distortions, and at times delusions; after 24 hours these gradually subsided.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 87.1
2. Boiling point (760 mm Hg): 166 C (331 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of dimethyl acetamide): 3.0
5. Melting point: −20 C (−4 F)
6. Vapor pressure at 20 C (68 F): 1.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Less than 0.17

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 350 C (662 F) cause decomposition and development of pressure in closed containers.
2. Incompatibilities: Contact with carbon tetrachloride and other halogenated compounds, particularly when in contact with iron, may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as dimethylamine and carbon monoxide) may be released in a fire involving dimethyl acetamide.
4. Special precautions: Dimethyl acetamide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 70 C (158 F) (open cup)
2. Autoignition temperature: 490 C (914 F)
3. Flammable limits in air, % by volume: Lower: 1.8 (at 212 F); Upper: 11.5 (at 320 F)
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide. Do not use halogenated extinguishing media.

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: Grant states that "on decomposition, it is said to emit fumes which are highly irritating to the eyes and mucous membranes." He reports that it causes mild, reversible injury graded 3 on a scale of 10 when tested on rabbit eyes.
3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dimethyl acetamide vapors using a silica gel tube, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethyl acetamide may be used. An analytical method for dimethyl acetamide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid dimethyl acetamide.
- Clothing contaminated with dimethyl acetamide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethyl acetamide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dimethyl acetamide, the person performing the operation should be informed of dimethyl acetamide's hazardous properties.
- Where exposure of an employee's body to dimethyl acetamide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with dimethyl acetamide should be removed immediately and not reworn until the dimethyl acetamide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dimethyl acetamide may contact the eyes.

SANITATION

- Skin that becomes contaminated with dimethyl acetamide should be immediately washed or showered to remove any dimethyl acetamide.
- Eating and smoking should not be permitted in areas where liquid dimethyl acetamide is handled, processed, or stored.
- Employees who handle liquid dimethyl acetamide should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethyl acetamide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a spinning solvent for synthetic fibers; as a solvent for film casting and top coating resins	Local exhaust ventilation; personal protective equipment
Use as a reaction medium and catalyst; as an extraction solvent for recovery and purification of butadiene; use as a crystallization and purification solvent; as a paint stripping solvent; during recovery and purification from top coating, film casting, spinning, and chemical processes	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dimethyl acetamide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dimethyl acetamide gets on the skin, immediately flush the contaminated skin with water. If liquid dimethyl acetamide soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of dimethyl acetamide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid dimethyl acetamide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dimethyl acetamide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Dimethyl acetamide may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR DIMETHYL ACETAMIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
100 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
400 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 400 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dimethyl acetamide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 400 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Dimethylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2NH$
- Synonyms: Dimethylamine, anhydrous
- Appearance and odor: Colorless liquid or gas with a pungent, fishy, or ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylamine is 10 parts of dimethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 18 milligrams of dimethylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylamine can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Dimethylamine vapor may cause irritation of the lungs, nose, throat, and eyes. It may cause coughing and sneezing. Contact with the liquid may cause skin and eye burns.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethylamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from dimethylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of dimethylamine might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Dimethylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Dimethylamine is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Dimethylamine gas is a severe respiratory, eye, and mucous membrane irritant in animals. Animals repeatedly exposed to concentrations of approximately 100 to 200 ppm for 18-20 weeks showed marked irritation of the respiratory tract with pulmonary edema as well as hepatic injury, including centrolobular necrosis; corneal injury was observed in guinea pigs and rabbits after 9 days of exposure. Various species survived 5 ppm of continuous exposure for 90 days without signs of toxicity, but at autopsy some showed mild inflammatory changes in the lungs. A drop of undiluted dimethylamine placed on a rabbit's cornea caused the cornea to become as white as the sclera in 1 minute. Both the liquid and the vapor are highly irritating to the eyes and may result in loss of visual acuity. Dermatitis and conjunctivitis are occasionally observed in chemical workers after prolonged exposure to the gas. No sys-

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temic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 45.1
  2. Boiling point (760 mm Hg): 6.9 C (44.4 F)
  3. Specific gravity (water = 1): 0.68 (liquid at 0 C)
  4. Vapor density (air = 1 at boiling point of dimethylamine): 1.6
  5. Melting point: −92 C (−134 F)
  6. Vapor pressure at 20 C (68 F): 1.72 atm.
  7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
  8. Evaporation rate (butyl acetate = 1): Greater than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers, chlorine, and mercury may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dimethylamine.
  4. Special precautions: Liquid dimethylamine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Not pertinent (gas)
  2. Autoignition temperature: 402 C (755 F)
  3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 14.4
  4. Extinguishant: Stop flow of gas.
- **Warning properties**
  1. Odor Threshold: Summer reports that the odor threshold of dimethylamine is 6 ppm, and May reports two odor thresholds, .021 and 23 ppm.
  2. Eye Irritation Level: The *Documentation of TLV's* reports that dimethylamine irritates mucous membranes. Repeated exposures of guinea pigs and rabbits to concentrations of 183 to 97 ppm dimethylamine have resulted in corneal injury. There is no available information on the threshold of eye irritation.
  3. Other Information: The *Documentation of TLV's* states that dimethylamine is a mucous membrane irritant and a respiratory tract irritant. The thresholds of irritation are not given.
  4. Evaluation of Warning Properties: Since the odor threshold ranges between one-five hundredth of the permissible exposure limit and approximately twice the permissible exposure limit, dimethylamine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors in a silica gel tube, followed by desorption with sulfuric acid in methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethylamine may be used. An analytical method for dimethylamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid dimethylamine.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing dimethylamine.
- Clothing wet with solutions containing dimethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to

remove the dimethylamine, the person performing the operation should be informed of dimethylamine's hazardous properties.

- Where there is any possibility of exposure of an employee's body to liquid dimethylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid solutions of dimethylamine should be removed promptly and not reworn until the dimethylamine is removed from the clothing.
- Any clothing which becomes wet with liquid dimethylamine or liquid solutions of dimethylamine should be removed immediately and not reworn until the dimethylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid dimethylamine or solutions containing dimethylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid dimethylamine or solutions containing dimethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid dimethylamine should be immediately washed or showered to remove any dimethylamine.
- Skin that becomes contaminated with solutions containing dimethylamine should be promptly washed or showered to remove any dimethylamine.
- Employees who handle dimethylamine or solutions containing dimethylamine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of spinning solvents for acrylic and polymeric fibers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as raw material in synthesis of agricultural chemicals; vulcanization accelerators for sulfur-cured rubber; softeners, lubricants; textile waterproofing agents; cationic surfactants; pharmaceuticals; detergents and soaps; as an antioxidant	Process enclosure; general dilution ventilation; personal protective equipment
Use as a general solvent; acid gas absorbent and flotation agent in manufacture of dyes and in electroplating	Process enclosure; general dilution ventilation; personal protective equipment
Use as photographic chemical, plasticizer, and ion exchange agent	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a stabilizer in natural rubber latex	Process enclosure; general dilution ventilation; local exhaust ventilation
Use as a stabilizer for certain types of resins (polymerization inhibitor)	General dilution ventilation; local exhaust ventilation
Use as a retarder in spinning bath of rayon (for tire cord)	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a component of rocket propellants; as an antiknock agent in other fuels	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dimethylamine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dimethylamine gets on the skin, immediately flush the contaminated skin with water. If dimethylamine soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of dimethylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dimethylamine has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dimethylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

- Waste disposal method:

Dimethylamine may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DIMETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
500 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) which provides protection against dimethylamine. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against dimethylamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against dimethylamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

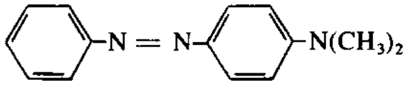
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
4-DIMETHYLAMINOAZOBENZENE
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 4-dimethylaminoazobenzene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{14}H_{15}N_3$
- **Structure:**



- **Synonyms:** N,N-Dimethyl-4-aminoazobenzene; N,N-dimethyl-4-(phenylazo)-benzenamine; p-dimethylaminoazobenzene; N,N-dimethyl-p-phenylazoaniline; benzeneazodimethylaniline; methyl yellow; DAB
- **Identifiers:** CAS 60-11-7; RTECS BX7350000; DOT not assigned.
- **Appearance:** Yellow leaf-shaped crystals

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 225.32
2. Boiling point (at 760 mmHg): Sublimes
3. Vapor density (air = 1 at boiling point of 4-dimethylaminoazobenzene): 7.78
4. Melting point: 116 °C (240 °F)
5. Vapor pressure: Negligible
6. Insoluble in water

- **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 4-dimethylaminoazobenzene.

- **Flammability**

Extinguishant: Alcohol foam, carbon dioxide, or dry chemical

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 4-dimethylaminoazobenzene; however, the OSHA standard requires implementation of stringent controls wherever 4-dimethylaminoazobenzene or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-dimethylaminoazobenzene are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1015, 4-Dimethylaminoazobenzene. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have a threshold limit value (TLV®) for 4-dimethylaminoazobenzene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

4-Dimethylaminoazobenzene may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

Effects on animals: Acute or oral administration of 4-dimethylaminoazobenzene to rats caused liver degeneration. Subchronic and chronic intraperitoneal injection or oral administration of 4-dimethylaminoazobenzene to rats produced liver cirrhosis and cancer, and chronic dermal exposure produced skin cancer. Chronic oral administration of 4-dimethylaminoazobenzene to dogs produced bladder cancer. 4-Dimethylaminoazobenzene has been reported to cause skeletal defects in mice when administered at single doses during embryogenesis and also to cause the production of abnormal sperm in mice.

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- **Signs and symptoms of exposure**

Long-term (chronic): Exposure to 4-dimethylaminoazobenzene can cause contact dermatitis, weakness, dizziness, a feeling of euphoria, shortness of breath, irregular muscular action, and a bluish discoloration of skin and mucous membranes (due to methemoglobinemia).

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 4-dimethylaminoazobenzene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, skin, and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 4-dimethylaminoazobenzene.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin or liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 4-dimethylaminoazobenzene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver, skin, and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 4-dimethylaminoazobenzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

- **Sentinel health events**

Acute and delayed-onset SHE's include: methymoglobinemia.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 4-dimethylaminoazobenzene dust with glass-fiber filters and Gas-Chrom P sorbent followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-dimethylaminoazobenzene may also be used if available. A detailed sampling and analytical method for 4-dimethylaminoazobenzene may be found in the *NIOSH Manual of Analytical Methods* (method number 284).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 4-dimethylaminoazobenzene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 4-dimethylaminoazobenzene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 4-dimethylaminoazobenzene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 4-dimethylaminoazobenzene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-dimethylaminoazobenzene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 4-dimethylaminoazobenzene from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1015:

Areas where 4-dimethylaminoazobenzene is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers are permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 4-dimethylaminoazobenzene, including local and systemic toxicity, the specific nature of the operations which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 4-dimethylaminoazobenzene which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-dimethylaminoazobenzene into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-dimethylaminoazobenzene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 4-dimethylaminoazobenzene shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 4-dimethylaminoazobenzene from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-dimethylaminoazobenzene may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 4-dimethylaminoazobenzene

Operations	Controls
During use in research and laboratory facilities; during use as a coloring agent for polishes, waxes, polystyrene, petroleum, and soap	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 4-dimethylaminoazobenzene, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 4-dimethylaminoazobenzene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-dimethylaminoazobenzene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 4-dimethylaminoazobenzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-dimethylaminoazobenzene gets on the skin, wash it immediately with soap and water. If 4-dimethylaminoazobenzene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 4-dimethylaminoazobenzene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 4-dimethylaminoazobenzene may be collected and placed in an appropriate container.
3. 4-Dimethylaminoazobenzene solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of 4-dimethylaminoazobenzene are prohibited by OSHA.
4. For small quantities of liquids containing 4-dimethylaminoazobenzene, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing 4-dimethylaminoazobenzene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 4-dimethylaminoazobenzene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Dimethylaniline

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5N(CH_3)_2$
- Synonyms: N,N-dimethylaniline
- Appearance and odor: Straw to brown-colored liquid with a characteristic amine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylaniline is 5 parts of dimethylaniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of dimethylaniline per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylaniline can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to dimethylaniline may affect the ability of the blood to carry oxygen. The earliest effect may be a bluish color of the skin, especially the lips. If the lack of oxygen becomes severe, a person may have drowsiness, headache, nausea, and vomiting. If oxygen lack is very severe, it may cause unconsciousness and even death.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethylaniline.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethylaniline at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, kidneys, liver, and cardiovascular system should be stressed.

—A complete blood count: Dimethylaniline has been shown to cause methemoglobinemia. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Dimethylaniline absorption, whether from inhalation of the vapor or by skin absorption of the liquid, causes anoxia due to the formation of methemoglobin. In dogs, the repeated subcutaneous injection of 1.5 g caused vomiting, weakness, cyanosis, methemoglobinemia, and hyperglobulinemia. It is said to be less toxic than aniline as regards methemoglobin formation but more of a central nervous system depressant. The liquid caused moderate injury in the eye of a rabbit.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 121
2. Boiling point (760 mm Hg): 192.8 C (379 F)
3. Specific gravity (water = 1): 0.96
4. Vapor density (air = 1 at boiling point of dimethylaniline): 4.2
5. Melting point: 2.5 C (36 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F):

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

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8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause violent spattering.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dimethylaniline.

4. Special precautions: Liquid dimethylaniline will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 62.8 C (145 F) (closed cup)

2. Autoignition temperature: 371 C (700 F)

3. Flammable limits in air, % by volume: Lower: 1.0 (calculated at flash point)

4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dimethylaniline.

2. Eye Irritation Level: Dimethylaniline vapor is not known to be an eye irritant. Grant reports that "in only one instance has it been involved in an ocular disturbance," and in this instance, it is not known if the disturbance should be attributed to the inhalation of phenol, which was also present, or dimethylaniline.

3. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of dimethylaniline to air concentrations, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dimethylaniline vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethylaniline may be used. An analytical method for dimethylaniline is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid dimethylaniline, where skin contact may occur.
- Clothing contaminated with dimethylaniline should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethylaniline from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dimethylaniline, the person performing the operation should be informed of dimethylaniline's hazardous properties.
- Where exposure of an employee's body to liquid dimethylaniline may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with dimethylaniline should be removed immediately and not reworn until the dimethylaniline is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dimethylaniline may contact the eyes.

SANITATION

- Skin that becomes contaminated with dimethylaniline should be immediately washed or showered with soap or mild detergent and water to remove any dimethylaniline.

- Eating and smoking should not be permitted in areas where liquid dimethylaniline is handled, processed, or stored.
- Employees who handle liquid dimethylaniline should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethylaniline may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of dye and dye intermediates; synthesis of explosives; pharmaceuticals; polyester resin systems; and intermediates for vanillin	Process enclosure; local exhaust ventilation; personal protective equipment
Use in absorption of sulfur dioxide	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid dimethylaniline gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dimethylaniline gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid dimethylaniline soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of dimethylaniline, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid dimethylaniline has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid dimethylaniline is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Dimethylaniline may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on dimethylaniline, look up dimethylaniline in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR DIMETHYLANILINE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dimethyl-1,2-Dibromo-2,2-Dichloroethyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3O)_2P(O)OCHBrCBrCl_2$ or $C_4H_7Br_2Cl_2O_4P$
- Synonyms: Naled; 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate; Dibrom
- Appearance and odor: Colorless solid or straw-colored liquid with a slightly pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate is 3 milligrams of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: If vapors of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate are inhaled, effects on the respiratory system and the eyes are the first to appear. These include tightness of the chest, wheezing, cough, excessive salivation, nasal discharge, aching in and behind the eyes, blurred vision, tearing, and headache. After swallowing the liquid, intestinal effects include loss of appetite, nausea, vomiting, cramps, and diarrhea. If spilled on the skin, it may cause itching, redness, and irritation. On being absorbed through the skin, this chemical may cause twitching and sweating at the site of absorption. If splashed in the eye, it may cause irritation. Severe intoxication, which may occur from breathing this chemical, swallowing it, or absorbing it through the skin or eye, may cause lightheadedness, slurred speech, muscle twitching, irregular heart beat, convulsions, paralysis, coma, and death.

2. Long-term Exposure: Repeated exposure to levels of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate may make a person more susceptible to the effects of this and related chemicals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of skin sensitization to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Cholinesterase determination: Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and erythrocytes should be determined by using medically acceptable biochemical assays prior to any exposure.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed semiannually or at any time overexposure is suspected or signs or symptoms of toxicity occur.

- **Summary of toxicology**

This substance is an anticholinesterase agent; absorption may occur from inhalation of the vapor, by skin absorption, or ingestion of the liquid. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine in the nervous system, skeletal and smooth muscles, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms occurs promptly, and almost always within 12 hours. After inhalation of the vapor, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion of the liquid, gastrointestinal effects such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption of the liquid, localized sweating and muscular fasciculations in the immediate area occur, usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is enhanced by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels and cardiac irregularities including complete heart block may occur, but these are often reversed by the establishment of adequate pulmonary ventilation. In nonfatal cases, complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for long periods after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects. Dermatitis occurred on the arms, face, neck, and abdomen of 9 of 12 persons working in a field of flowers which had been freshly sprayed with a solution of Dibrom; three of four workers patch-tested were positive to a 60% solution of Dibrom in xylene and negative to xylene alone. The liquid in the eye is expected to cause injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 381
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.97
4. Vapor density (air = 1 at boiling point of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate): Not
5. Melting point: 27 C (81 F)
6. Vapor pressure at 20 C (68 F): 0.0002 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble, decomposes about 10% per day in water
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, hydrogen chloride, phosphoric acid, and carbon monoxide) may be released when dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate decomposes.
4. Special precautions: Liquid dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Dibrom is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may

be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, where skin contact may occur.
- If employees' clothing may have become contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liqcontaining dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which may have become contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, the person performing the operation should be informed of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate's hazardous properties.
- Non-impervious clothing which becomes contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be removed immediately and not reworn until the dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be immediately washed or showered with soap or mild detergent and water to remove any dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate.
- Workers subject to skin contact with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should wash any areas of the body which may have contacted dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate at the end of each work day.
- Eating and smoking should not be permitted in areas where dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate are handled, processed, or stored.
- Employees who handle dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate may occur and control methods which may be effective in each case:

Operation	Controls
Use as an agricultural insecticide and acaricide applied to fruit, vegetables, and agronomic crops; use in domestic, commercial, and agricultural premises	Personal protective equipment
Use in compounding water-base paints and floor polishes for insecticidal properties	Process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal methods:

Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate may be disposed of:

1. If in the solid form, by disposing in a secured sanitary landfill.
2. If in the liquid form, by absorbing in vermiculite, dry sand, earth, or a similar material, and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR DIMETHYL-1,2-DIBROMO-2,2-DICHLOROETHYL PHOSPHATE

Condition	**Minimum Respiratory Protection* Required Above 3 mg/m³**
Particulate Concentration	
15 mg/m³ or less	Any dust and mist respirator, except single-use, including pesticide respirators which meet the requirements of this class.
30 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator, including pesticide respirators which meet the requirements of this class. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
150 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1800 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode.
Greater than 1800 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dimethyl Formamide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HCON(CH_3)_2$
- Synonyms: N,N-dimethyl formamide; DMF
- Appearance and odor: Colorless liquid with a faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethyl formamide is 10 parts of dimethyl formamide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of dimethyl formamide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethyl formamide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of dimethyl formamide or skin contact with dimethyl formamide may cause abdominal distress, colicky abdominal pain, loss of appetite, nausea, vomiting, constipation, diarrhea, facial flushing (especially after drinking alcohol), liver injury, agitation, and increased blood pressure. Skin contact may cause skin irritation.

2. Long-term Exposure: Repeated or prolonged skin contact with dimethyl formamide may cause a rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethyl formamide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethyl formamide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver, kidneys, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Since liver damage has been observed in humans exposed to dimethyl formamide, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Dimethyl formamide vapor is toxic to the liver. Repeated exposure of rats to concentrations of 100 to 450 ppm for 4 months resulted in necrosis of the liver and mild kidney damage. Animal studies have shown toxic effects at high levels on multiple organ systems. Thirteen workers exposed to concentrations below 20 ppm and occasionally to higher levels for up to 32 weeks complained of nausea, vomiting, and colic; some cases of hepatomegaly were detected. A worker who was splashed with the liquid over 20% of his body surface initially suffered only dermal irritation and hyperemia; abdominal pain began 62 hours after the exposure and became progressively more severe, with vomiting; the blood pressure was elevated to 190/100; the effects gradually subsided and were entirely abated by the 7th day after the exposure. Some workers have noted flushing of the face after inhalation of the vapor, especially with coincident ingestion of alcoholic bever-

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ages. Effects resemble those of porphyria. Prolonged or repeated skin contact with the liquid may cause dermatitis as a result of a defatting action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 73.1
2. Boiling point (760 mm Hg): 153 C (307 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of dimethyl formamide): 2.5
5. Melting point: −61 C (−78 F)
6. Vapor pressure at 20 C (68 F): 2.7 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 0.17

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 350 C (662 F) may cause decomposition and development of pressure in closed containers.

2. Incompatibilities: Contact with carbon tetrachloride and other halogenated compounds, particularly when in contact with iron, or contact with strong oxidizers may cause fires and explosions. Dimethyl formamide may react vigorously with alkylaluminums when the latter are used as polymerization catalysts.

3. Hazardous decomposition products: Toxic gases and vapors (such as dimethylamine and carbon monoxide) may be released in a fire involving dimethyl formamide.

4. Special precautions: Dimethyl formamide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 58 C (136 F) (closed cup)
2. Autoignition temperature: 445 C (833 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 15.2 (at 100 C (212 F))
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide. Do not use halogenated extinguishing media.

- **Warning properties**

1. Odor Threshold: According to the Department of Transportation's *Hazardous Chemical Data*, the odor threshold of dimethyl formamide is 100 ppm.

2. Eye Irritation Level: According to Deichmann and Gerarde, dimethyl formamide "is highly irritating to skin, eyes, and mucous membranes." No quantitative information is available concerning the threshold levels of irritation.

3. Evaluation of Warning Properties: Since the odor threshold of dimethyl formamide is 10 times higher than the permissible exposure limit, and since no other quantitative information is available relating to warning properties to air concentrations, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dimethyl formamide vapors using a silica gel tube, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethyl formamide may be used. An analytical method for dimethyl formamide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid dimethyl formamide.
- Non-impervious clothing which becomes contaminated with dimethyl formamide should be removed

promptly and not reworn until the dimethyl formamide is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid dimethyl formamide may contact the eyes.

SANITATION

- Skin that becomes contaminated with dimethyl formamide should be promptly washed or showered to remove any dimethyl formamide.
- Employees who handle liquid dimethyl formamide should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethyl formamide may occur and control methods which may be effective in each case:

Operation	Controls
Use as resin and polymer solvent as spinning solvent for acrylic fibers; booster solvent in coating, printing, and adhesive formulations	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate, catalyst and reaction medium in chemical manufacturing industry	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a selective absorption and extraction solvent for recovery, purification absorption, separation and desulfurization of non-paraffinics from paraffin hydrocarbons	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of paint stripper component for removal of vinyl films, epoxy coatings, and varnish finishes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in pigment and dye industry to improve dyeing properties; use as solvent of dyes and pigments for use with textiles, wood, leather, films, paper, and plastics; use as a crystallization solvent in pharmaceutical industry; use as a solvent for carbonaceous deposit cleaning	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous applications for high-voltage capacitors, oil sludge dispersing agent, antistall gasoline additive, quench for tinned parts and wood pulping	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid dimethyl formamide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dimethyl formamide gets on the skin, promptly flush the contaminated skin with water. If liquid dimethyl formamide soaks through the clothing, remove the clothing promptly and flush the skin with water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of dimethyl formamide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid dimethyl formamide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify some-

one else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid dimethyl formamide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Dimethyl formamide should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of dimethyl formamide vapors are permitted.

- Waste disposal methods:

Dimethyl formamide may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DIMETHYL FORMAMIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
100 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3500 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3500 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dimethyl formamide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 3500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR

1,1-DIMETHYLHYDRAZINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 1,1-dimethylhydrazine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2N_2H_8$
- **Structure:** $(CH_3)_2N\text{-}NH_2$
- **Synonyms:** Asymmetric dimethylhydrazine; dimazine; dimethylhydrazine; N,N-dimethylhydrazine; dimethylhydrazine unsymmetrical; DMH; UDMH
- **Identifiers:** CAS 157-14-7; RTECS MV2450000; DOT 1163, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid that fumes in air, gradually turns yellow, and has a fishy or ammonialike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60.12
2. Boiling point (at 760 mmHg): 63.9 °C (147 °F)
3. Specific gravity (water = 1): 0.782
4. Vapor density (air = 1 at boiling point of 1,1-dimethylhydrazine): 2.08
5. Melting point: -58 °C (-72 °F)
6. Vapor pressure at 25 °C (77 °F): 156.8 mmHg
7. Miscible with water
8. Evaporation rate (butyl acetate = 1): 8.6
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 20.6% (206,000 ppm)
10. Ionization potential: 7.46 eV

- **Reactivity**

1. Incompatibilities: 1,1-dimethylhydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving 1,1-dimethylhydrazine.
3. Caution: 1, 1-Dimethylhydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -15 °C (5 °F) (closed cup)
2. Autoignition temperature: 249 °C (480 °F)
3. Flammable limits in air, % by volume: Lower, 2; Upper, 95
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Caution: 1,1-dimethylhydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

1. Odor threshold: 6-14 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 1,1-dimethylhydrazine is 0.5 parts of 1,1-dimethylhydrazine per million parts of air (ppm) [1 milligram of 1,1-dimethylhydrazine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that 1,1-dimethylhydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.06 ppm (0.15 mg/m^3) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Con-

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

ference of Governmental Industrial Hygienists (ACGIH) has designated 1,1-dimethylhydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 0.5 ppm (1.0 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for 1, 1-dimethylhydrazine

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	0.5	1
NIOSH REL (Ca)† Ceiling (120 min)	0.06	0.15
ACGIH TLV® TWA (Skin) (A2)§	0.5	1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1-Dimethylhydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of 1,1-dimethylhydrazine by mice, rats, or dogs caused central nervous system (CNS) stimulation, respiratory distress, convulsions, and death. Repeated daily exposure of dogs to 1,1-dimethylhydrazine vapor produced CNS depression, salivation, vomiting, diarrhea, loss of muscular coordination (ataxia), convulsive seizures, and hemolytic anemia. Chronic oral administration of 1,1-dimethylhydrazine to mice caused tumors of the blood vessels, lungs, kidneys, and liver.
2. *Effects on humans:* Exposure of workers to 1,1-dimethylhydrazine has caused increased blood pressure, fatty infiltration of the liver, impaired liver function (resulting in elevated serum glutamic-pyruvic transaminase levels, respiratory distress, hemolysis, and reduced oxygen supply to tissues (anoxia).

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure can cause a choking sensation, chest pain, breathing difficulty (dyspnea), lethargy, nausea, vomiting, and irritation of the skin, eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to 1,1-dimethylhydrazine can cause pulmonary irritation, conjunctivitis, and gastrointestinal irritation.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 1,1-dimethylhydrazine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, red blood cells, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis. A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 1,1-dimethylhydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to 1,1-dimethylhydrazine.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 1,1-dimethylhydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, kidneys, red blood cells, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 1,1-dimethylhydrazine may cause diseases of prolonged induction latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of 1,1-dimethylhydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting 1,1-dimethylhydrazine vapors with sulfuric acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure 1,1-dimethylhydrazine may also be used if available. A detailed sampling and analytical method for 1,1-dimethylhydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions. Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with 1,1-dimethylhydrazine.

SANITATION

Clothing which is contaminated with 1,1-dimethylhydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dimethylhydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 1,1-dimethylhydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with 1,1-dimethylhydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 1,1-dimethylhydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 1,1-dimethylhydrazine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 1, 1-dimethylhydrazine

Operations	Controls
During the formulation of and use in jet and rocket propellants	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of 1,1-dimethylhydrazine and during maintenance of manufacturing and storage equipment	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the chemical synthesis of catalysts, automotive antifreeze, pharmaceuticals, dyestuffs, and stabilizing agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the formulation of photographic developers and the processing of styrene-butadiene rubber	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 1,1-dimethylhydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 1,1-dimethylhydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 1,1-dimethylhydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 1,1-dimethylhydrazine gets on the skin, wash it immediately with soap and water. If 1,1-dimethylhydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 1,1-dimethylhydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing 1,1-dimethylhydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing 1,1-dimethylhydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. 1,1-Dimethylhydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for 1, 1-dimethylhydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Dimethylphthalate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_{10}O_4$
- Synonyms: DMP
- Appearance and odor: Colorless, oily liquid with a slight ester odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylphthalate is 5 milligrams of dimethylphthalate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylphthalate can affect the body if it is swallowed, is inhaled, or comes in contact with the eyes.

- **Effects of overexposure**

Overexposure to hot vapors or mists of dimethylphthalate may cause irritation of the nasal passages and the mouth and throat. Eye contact with liquid dimethylphthalate causes pain. If swallowed, dimethylphthalate may cause irritation of the stomach, dizziness, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethylphthalate.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to dimethylphthalate at potentially hazardous levels.

- **Summary of toxicology**

Extensive experience with dimethylphthalate as an insect repellent has shown that it is relatively nonirritating to the skin, eyes, and mucous membranes. Aerosols from heated dimethylphthalate may cause irritation of the eyes and upper respiratory tract. In one fatal case of suicidal ingestion of a mixture containing dimethylphthalate and ketone peroxides, the principal toxic symptoms were marked esophagitis and gastritis with hemorrhage. Animal experiments to determine dermal and oral toxicity of dimethylphthalate showed that extremely high doses were considered necessary to produce toxic effects. Dimethylphthalate was found to be teratogenic by intraperitoneal injection of doses representing 1/10, 1/5, and 1/3 of the LD50 value into female rats at the 5th, 10th, and 15th day of gestation. This probably is of no significance in industrial exposures.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 194
2. Boiling point (760 mm Hg): 285 C (545 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of dimethylphthalate): 6.7
5. Melting point: 0 to 2 C (32 to 36 F)
6. Vapor pressure at 100.3 C (212 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.04
8. Evaporation rate (methyl acetate = 1): Almost zero

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dimethylphthalate.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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4. Special precautions: None

- **Flammability**

1. Flash point: 146 C (295 F) (closed cup)
2. Autoignition temperature: 556 C (1032 F)
3. Flammable limits in air, % by volume: Lower: 1.2 (calculated at flash point)
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

According to Grant, contact of dimethylphthalate with the eye "produces considerable pain, but causes either no damage or only slight reversible disturbance of the epithelium." Air concentrations which would produce this effect are not given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for dimethylphthalate had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use splash-proof safety goggles where liquid dimethylphthalate may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethylphthalate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a plasticizer in compounding of plastics, primarily cellulose acetate, nitrocellulose, ethylcellulose, cellulose acetate butyrate, polystyrene, polyvinyl acetate, polyvinyl butyral, and polyvinyl chloride	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of surface coatings containing plasticized resins and polymers, including furniture lacquers, printing inks, textile and paper coatings, and moisture-proof coatings for cellophane	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during molding, casting, extrusion, or other processing of heated, plasticized resins and polymers in manufacture of plastic articles	Local exhaust ventilation; general dilution ventilation
Use in spray (or dip applications or any method involving heat) of surface coatings containing plasticized resins and polymers, including furniture lacquers, printing inks, textiles and paper coatings, and moisture-proof coatings on cellophane	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a plasticizer in compounding of nitrile and neoprene rubber and chlorinated rubber	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in spray or other applications of adhesives containing plasticizer, including polyvinyl acetate adhesives for cellulose acetate films, covering cut-out windows in cartons, or laminating cellulose acetate film to paper	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during processing of heated plasticized nitrile, neoprene, and chlorinated rubber into manufactured articles	Local exhaust ventilation; general dilution ventilation
Use during preparation of adhesives containing plasticizer, including polyvinyl acetate adhesives for cellulose film	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of insect repellant formulations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dimethylphthalate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention if any discomfort continues. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dimethylphthalate saturates the clothing, remove and clean the clothing before wearing it again. Wash any dimethylphthalate from the skin regularly, particularly when there has been much skin contact. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of dimethylphthalate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dimethylphthalate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing respiratory protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dimethylphthalate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

- Waste disposal methods:

Dimethylphthalate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR DIMETHYLPHTHALATE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
250 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
9300 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 9300 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dimethylsulfate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2SO_4$
- Synonyms: Methyl sulfate
- Appearance and odor: Colorless, oily liquid with a faint onion odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylsulfate is 1 part of dimethylsulfate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of dimethylsulfate per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for dimethylsulfate a Threshold Limit Value of 0.1 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylsulfate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may readily enter the body through the skin.

- **Effects of overexposure**

Dimethylsulfate vapor is an extremely severe irritant of the eyes, respiratory tract, and skin. While exposure often produces no immediate effects other than slight eye and nose irritation, after a period of up to 10 hours or more, headache and giddiness with intense pain on exposure to light may occur. This is usually followed by inflammation of the throat and voice box, difficulty in speaking, difficulty in swallowing, cough, tightness of the chest, shortness of breath, a blue coloration of the skin, vomiting, diarrhea, and painful urination. Other effects are delirium, fever, yellow jaundice, and bloody urine. Liver and kidney damage may occur. If the liquid is swallowed, in addition to causing burns of the throat and stomach, the above effects may occur. Contact of the liquid with the eyes and skin will cause severe burns. Animal experiments have shown that this chemical may cause cancer in animals and their offspring.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dimethylsulfate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethylsulfate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, liver, kidneys, and central nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to dimethylsulfate, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to dimethylsulfate, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—14" x 17" chest roentgenogram: Dimethylsulfate causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Dimethylsulfate is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

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2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Dimethylsulfate vapor is an extremely severe irritant of the eyes, mucous membranes, and skin; it is carcinogenic in rats. It has a strong vesicant action and rapidly hydrolyzes in the presence of water to produce sulfuric acid and methanol. It caused malignant tumors in rats in various organs by inhalation, subcutaneous injection, and following prenatal exposure. A single intravenous dose of 20 mg/kg given to 8 pregnant rats on day 15 of gestation induced malignant tumors, including 3 tumors of the nervous system, in 7 of 59 offspring which were observed for over 1 year. The LC50 in rats was 75 ppm for 18 minutes; autopsy findings were marked pulmonary edema, pulmonary emphysema, peribronchitis, and focal necrosis of the liver. Several human deaths have occurred from occupational exposure. While exposure of humans often produces no immediate effects other than occasional slight eye and nose irritation, after a latent period of up to 10 hours or more, there is onset of headache and giddiness with intense conjunctival irritation, photophobia, and periorbital edema; this is usually followed by inflammation of the pharyngo-laryngeal mucosa, dysphonia, aphonia, dysphagia, productive cough, oppression in the chest, dyspnea and cyanosis; vomiting and diarrhea may intervene. Dysuria may occur for 3 to 4 days; there may be persistence of laryngeal edema for up to 2 weeks and of photophobia for several months. Other effects are delirium, fever, icterus, albuminuria, and hematuria. Contact of the liquid with the eyes or skin will cause very severe burns due to its powerful vesicant action. In one incident of moderate skin contact with the liquid, generalized intoxication occurred even though there was prompt treatment of the skin; the vapor was inhaled for no more than a few minutes.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 126.1
2. Boiling point (760 mm Hg): 188.8 C (372 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of dimethylsulfate): 4.35
5. Melting point: −31.8 C (−25 F)
6. Vapor pressure at 20 C (68 F): 0.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 2.8 (reacts slowly)
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Contact with water may allow formation of flammable concentrations of methyl alcohol.
2. Incompatibilities: Contact with strong oxidizers or with strong ammonia solutions may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfuric acid mist, methyl alcohol, and carbon monoxide) may be released in a fire involving dimethylsulfate.
4. Special precautions: Dimethylsulfate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 83.3 C (182 F) (closed cup)
2. Autoignition temperature: 187.8 C (370 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that "dimethylsulfate is a colorless, oily liquid, which is nearly odorless or which may have a faint onion-like odor."

2. Irritation Levels: Grant states that "injury of the eye by vapor of dimethylsulfate is a much more common industrial accident than injury by a splash of liquid, which is more easily prevented by goggles. Numerous instances of burns and poisoning from the vapor have been described. Also, in animal eyes the effects of the vapor have several times been studied and reproduced. Characteristically, during exposure to vapor of dimethylsulfate the patient or experimental animal is not aware of irritation or unpleasant sensation but begins to develop discomfort several hours later.

'Moeschlin in his book on poisonings particularly has placed great emphasis on the latent period that is characteristic of the action of dimethylsulfate vapors on the eyes, giving description of specific cases in which there were latent periods as long as six hours before severe inflammation of the eyes and respiratory tract developed. Browning in her book on toxicology has reviewed several of the reports in the literature of eye involvement from vapor exposure.

'Typical industrial exposure occurs when workmen pour dimethylsulfate from one container to another, with no irritation of eyes or nose, or no unpleasant odor to warn of danger. After several hours the eyes begin to feel irritated and have a sandy sensation. Photophobia and lacrimation develop; the lids become edematous and the conjunctiva hyperemic. The skin of the face and other exposed parts is reddened. The symptoms increase in intensity for several hours, and then superficial clouding and irregularity of the corneal epithelium may be seen. Associated with the ocular symptoms are temporary loss of smell and taste, with hoarseness and irritation of the respiratory passages which may become severe, and in the worst cases may develop into fatal pneumonia.

'The course of the eye injuries in the mildest cases may be spontaneous return to normal in a few days, or, in severe cases, gray necrosis of the epithelium, edema and infiltration of the corneal stroma, and permanent partial opacification may result."

No quantitative information is available concerning the levels of dimethylsulfate which produce eye irritation. The effects on the eyes are delayed.

3. Evaluation of Warning Properties: Since dimethylsulfate is "almost odorless," and since the irritant effects produced by this compound are delayed, dimethylsulfate is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for dimethylsulfate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid dimethylsulfate.
- Clothing contaminated with dimethylsulfate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethylsulfate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dimethylsulfate, the person performing the operation should be informed of dimethylsulfate's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid dimethylsulfate, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with dimethylsulfate should be removed immediately and not reworn until the dimethylsulfate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid dimethylsulfate contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid dimethylsulfate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with dimethylsulfate should be immediately washed or showered with soap or mild detergent and water to remove any dimethylsulfate.
- Employees who handle liquid dimethylsulfate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethylsulfate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a methylating agent in organic chemical industry for manufacture of esters, ethers, and amines	Enclosed system/ segregation; general dilution ventilation; personal protective equipment
Use in manufacture of dyes, dyestuffs, coloring agents, and perfumes; use in pharmaceutical industry as a solvent for separation/preparation of mineral oils	Enclosed system/ segregation; general dilution ventilation; personal protective equipment
Use during analysis of automobile fluids	Enclosed system/ segregation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid dimethylsulfate or strong concentrations of dimethylsulfate vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid dimethylsulfate or strong concentrations of dimethylsulfate vapors get on the skin, immediately flush the contaminated skin with large amounts of water. If liquid dimethylsulfate or strong concentrations of dimethylsulfate vapors penetrate through the clothing, remove the clothing immediately and flush the skin with large amounts of water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of dimethylsulfate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If dimethylsulfate has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the dimethylsulfate. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dimethylsulfate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Dimethylsulfate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 4, 1974.

RESPIRATORY PROTECTION FOR DIMETHYLSULFATE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
10 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against dimethylsulfate. Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dimethylsulfate; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DINITOLMIDE

INTRODUCTION

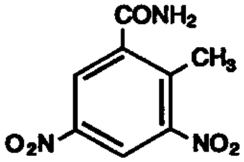
This guideline summarizes pertinent information about dinitolmide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8H_7N_3O_5$

- **Structure**



- **Synonyms**

Zoalene; 2-methyl-3,5-dinitrobenzamide; Coccidine A; Coccidot; dinitolmid; Zoamix; 3,5-dinitro-o-toluamide

- **Identifiers**

1. CAS No.: 148-01-6
2. RTECS No.: XS4200000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Dinitolmide is a noncombustible, yellowish, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 225.2
2. Boiling point: Data not available
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: 177°C (350.6°F)
6. Vapor pressure: Data not available

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7. Solubility: Very slightly soluble in water; soluble in acetone, acetonitrile, dioxane, and dimethylformamide.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving dinitolmide.

4. Special precautions: None reported.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for dinitolmide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving dinitolmide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dinitolmide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dinitolmide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for dinitolmide [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dinitolmide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of liver damage associated with exposure to dinitolmide [NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dinitolmide can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to dinitolmide causes methemoglobinemia and liver changes in animals. The oral LD$_{50}$ in rats is 600 mg/kg [NIOSH 1993]. Rats given a single 150-mg/kg oral dose of dinitolmide developed methemoglobinemia [Gosselin et al. 1984]. Rats fed 6 mg/kg dinitolmide daily for 2 years showed slightly increased liver weights and fatty liver changes in both sexes at autopsy [ACGIH 1991]. Rats fed 3 mg/kg/day showed no adverse effects on growth, mortality rate, tumor incidence, fertility, gestation, or viability [ACGIH 1991]. Beagle dogs fed 10 mg/kg/day for 1 year also showed no effects when evaluated on these measures [ACGIH 1991]. Dinitolmide is mutagenic in bacterial test systems [NIOSH 1993].

2. *Effects on Humans:* In contact with the skin, dinitolmide has caused allergic contact dermatitis in two female poultry attendants [ACGIH 1991]. No other reports on dinitolmide's effects in humans are available.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to dinitolmide have been reported in humans.

2. *Chronic exposure:* Chronic exposure to dinitolmide may cause allergic contact dermatitis. The signs and symptoms include redness, itching, and swelling (hives).

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dinitolmide or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve dinitolmide and lead to worker exposures to this substance:

—Use as a coccidiostat and food additive

The following methods are effective in controlling worker exposures to dinitolmide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dinitolmide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and liver.

  A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dinitolmide at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the skin or liver.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dinitolmide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dinitolmide on the skin or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dinitolmide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dinitolmide is made using a 37-mm glass fiber filter. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 240 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Laboratory In-House Methods File [ACGIH 1991].

PERSONAL HYGIENE

If dinitolmide contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dinitolmide should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles dinitolmide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dinitolmide or a solution containing dinitolmide is handled, processed, or stored.

STORAGE

Dinitolmide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of dinitolmide should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving dinitolmide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Use a clean shovel and gently place the spilled material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dinitolmide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dinitolmide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dinitolmide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dinitolmide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dinitolmide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing and gloves should be worn to prevent skin contact with dinitolmide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dinitolmide permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dinitolmide.

If dinitolmide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dinitolmide might contact the eyes (e.g., through dust particles). Eyewash fountains should be available within the immediate work area whenever the potential exists for eye contact with dinitolmide.

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Occupational Health Guideline for Dinitrobenzene (All Isomers)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Ortho: 1,2-$C_6H_4(NO_2)_2$; Meta: 1,3-$C_6H_4(NO_2)_2$; Para: 1,4-$C_6H_4(NO_2)_2$
- Synonyms: O-dinitrobenzene; 1,2-dinitrobenzene; m-dinitrobenzene; 1,3-dinitrobenzene; p-dinitrobenzene; 1,4-dinitrobenzene
- Appearance: Pale yellow solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dinitrobenzene is 1 milligram of dinitrobenzene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for dinitrobenzene a Threshold Limit Value of 0.15 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dinitrobenzene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It is readily absorbed through the skin, either as solid, liquid, or vapor. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

Dinitrobenzene may affect the ability of blood to carry oxygen. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. Consuming alcohol may make symptoms worse. Dinitrobenzene may also cause an unpleasant taste or burning sensation in the mouth, dry, throat, and thirst. The eyes, hair, and skin may become yellowish. Dinitrobenzene may cause reduced vision. In addition, liver damage may occur. Repeated or prolonged exposure to dinitrobenzene may cause anemia.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dinitrobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dinitrobenzene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, liver, cardiovascular system, and eyes should be stressed.

—A complete blood count: Dinitrobenzene has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Observe for Heinz bodies.

—Liver function tests: Since liver damage has been observed in humans exposed to dinitrobenzene, a profile of liver function should be performed by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Absorption of any isomer of dinitrobenzene, whether from inhalation of the vapor or dust or skin absorption

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Public Health Service Center for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

of the solid, causes anoxia due to the formation of methemoglobin; chronic exposure produces anemia. Exposed workers have complained of an unpleasant taste, burning sensation in the mouth, dry throat, and thirst. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is often recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. Until the methemoglobin concentration approaches approximately 40%, the individual may feel well, have no complaints, and may insist nothing is wrong. At methemoglobin concentrations of over 40%, there usually is weakness and dizziness; up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. The ingestion of alcohol has been reported to aggravate the toxic effects of dinitrobenzene. Chronic exposure of workers causes anemia; there are scattered reports of liver injury. Visual impairment has been reported in the form of reduced visual acuity and central scotomas, particularly for red and green colors; yellow discoloration of the conjunctiva and sclera is common. Yellow-brown discoloration of the hair and exposed skin of workers has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 168.1
2. Boiling point (760 mm Hg): Ortho: 318 C (604 F); Meta: 300 C (572 F); Para: 297 C (566 F)
3. Specific gravity (water = 1): Ortho: 1.59; Meta: 1.57; Para: 1.63
4. Vapor density (air = 1 at boiling point of dinitrobenzene): 5.8
5. Melting point: Ortho: 117 C (243 F); Meta: 90 C (194 F); Para: 173 C (343 F)
6. Vapor pressure at 20 C (68 F): All isomers: Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.01; Meta: 0.05; Para: 0.01
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Dinitrobenzene may detonate when subject to shock or when heated under confinement.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with caustics and metals such as tin and zinc may cause evolution of heat and increase in pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dinitrobenzene.
4. Special precautions: Liquid dinitrobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Explodes
2. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): Greater than 100 centimeters
2. Autoignition temperature: Data not available
4. Flammable limits in air, % by volume: Data not available
5. Extinguishant: None

- **Warning properties**

Grant states that "surface contact (with dinitrobenzene) may cause yellowing of the skin, and purportedly of the conjunctiva and cornea, but no original observations on corneal changes were found in the literature." According to Grant, "2,4-dinitrobenzene caused no inflammatory response when this substance was brought into contact with the uveal tract, retina, or conjunctiva" of guinea pigs.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for dinitrobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted

are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with dinitrobenzene or liquids containing dinitrobenzene, where skin contact may occur.
- If employees' clothing may have become contaminated with solid dinitrobenzene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with dinitrobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dinitrobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dinitrobenzene, the person performing the operation should be informed of dinitrobenzene's hazardous properties.
- Where exposure of an employee's body to liquids containing dinitrobenzene may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes wet with liquids containing dinitrobenzene should be removed immediately and non-impervious clothing which becomes contaminated with dinitrobenzene should be removed promptly and such clothing should not be reworn until the dinitrobenzene is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where dinitrobenzene or liquids containing dinitrobenzene may contact the eyes.

SANITATION

- Skin that becomes wet with liquids containing dinitrobenzene should be immediately washed or showered with soap or mild detergent and water to remove any dinitrobenzene.
- Skin that becomes contaminated with dinitrobenzene should be promptly washed or showered with soap or mild detergent and water to remove any dinitrobenzene.
- Workers subject to skin contact with dinitrobenzene should wash with soap or mild detergent and water any areas of the body which may have contacted dinitrobenzene at the end of each work day.
- Eating and smoking should not be permitted in areas where dinitrobenzene or liquids containing dinitrobenzene are handled, processed, or stored.
- Employees who handle dinitrobenzene or liquids containing dinitrobenzene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dinitrobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of dyes and dye intermediates; use in organic synthesis in chemical industry as photographic developers, and as explosives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in plastics industry as a substitute for camphor in production of celluloid; as a polymerization inhibitor	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an explosive by substituting for TNT; use in explosive shells	Material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dinitrobenzene or liquids containing dinitrobenzene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dinitrobenzene or liquids containing dinitrobenzene get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dinitrobenzene or liquids containing dinitrobenzene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of dinitrobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dinitrobenzene or liquids containing dinitrobenzene have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If dinitrobenzene is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other suitable material and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities may be reclaimed; however, if this is not practical, dissolve in fuel oil and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Dinitrobenzene may be disposed of:

1. By making packages of dinitrobenzene in paper or other flammable material and burning in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device.
2. By dissolving dinitrobenzene in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DINITROBENZENE (ALL ISOMERS)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator, except single-use.
10 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

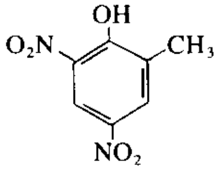
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DINITRO-ORTHO-CRESOL

INTRODUCTION

This guideline summarizes pertinent information about dinitro-ortho-cresol (DNOC) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_7H_6N_2O_5$
- **Structure:**



- **Synonyms:** DNOC; 2,4-dinitro-o-cresol; 4,6-dinitro-o-cresol; 3,5-dinitro-2-hydroxytoluene; 4,6-dinitro-2-methyl phenol; antinonin; capsine; chemsect DNOC
- **Identifiers:** CAS 534-52-1; RTECS GO9625000; DOT 2446, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Yellow, odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical Data**

1. Molecular weight: 198.13
2. Boiling point (at 760 mmHg): 312 °C (595 °F)
3. Vapor density (air = 1 at boiling point of DNOC): 6.8
4. Melting point: 85.8 °C (186 °F)
5. Vapor pressure at 20 °C (68 °F): 5.2×10^{-5} mmHg
6. Solubility in water, g/100 g water at 20 °C (68 °F): 0.01

- **Reactivity**

1. Incompatibilities: Heat and strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving DNOC.
3. Caution: DNOC is a combustible solid; DNOC dust may form explosive mixtures with air.

- **Flammability**

1. Minimum explosive dust concentration: 30 g/m^3
2. Minimum dust cloud ignition temperature: 340 °C (644 °F)
3. Extinguishant: Foam, dry chemical, or carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, DNOC should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DNOC is 0.2 milligram of DNOC per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 0.2 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.2 mg/m^3 (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for DNOC

	Exposure limits mg/m^3
OSHA PEL TWA (Skin)*	0.2
NIOSH REL TWA	0.2
ACGIH TLV® TWA (Skin)	0.2

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

DNOC may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

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National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of DNOC by cats produced increased white blood cell counts, decreased red blood cell counts, and decreased blood enzyme activities. Oral administration of DNOC to sheep caused toxic effects to the liver and kidneys. In mutagenicity tests, DNOC caused chromosome damage in the reproductive cells of male mice and DNA damage in bacteria.
2. *Effects on humans:* DNOC has caused increased metabolism, liver and kidney damage, brain hemmorhage with partial loss of circulation, and destruction of nerve sheaths. Chronic ingestion of therapeutic doses of DNOC has produced glaucoma and bilateral cataracts. The toxicity of DNOC is cumulative, and excretion is slow.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to DNOC can cause euphoria, headache, fatigue, nausea, flushed skin, jaundice, muscular incoordination, cough, fever, profuse sweating, excessive thirst, rapid respiration and heart rate, collapse, and coma. Irritation of the skin and eyes can also occur.
2. *Long-term (chronic):* Exposure to DNOC can cause restlessness, anxiety, weight loss, and jaundice.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to DNOC, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and endocrine systems (with particular attention to the thyroid gland).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DNOC at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include historical and physical or laboratory findings consistent with cataracts or chronic diseases of the skin or liver.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DNOC. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity or physiologic function of the eyes, skin, liver, kidneys, and nervous and endocrine systems (with particular attention to the thyroid gland) as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DNOC may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Cataracts.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to DNOC should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting DNOC with cellulose ester membrane filters followed by extraction with ethylene glycol and analysis by high pressure liquid chromatography. Detector tubes or other direct-reading devices calibrated to measure DNOC may also be used if available. A detailed sampling and analytical method for DNOC may be found in the *NIOSH Manual of Analytical Methods* (method number S166).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with DNOC.

Workers should be provided with and required to use dust- and splash-proof safety goggles where DNOC may come in contact with the eyes.

SANITATION

Clothing which is contaminated with DNOC should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of DNOC from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DNOC's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with DNOC should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DNOC should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DNOC may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for DNOC

Operations	Controls
During the manufacture and processing of DNOC	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During cleaning and maintenance of storage vessels	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a herbicide, insecticide, or fungicide	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DNOC, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DNOC gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to DNOC, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DNOC gets on the skin, wash it immediately with soap and water. If DNOC penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DNOC is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities of liquids containing DNOC, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from DNOC vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing DNOC may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. DNOC should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, DNOC may be collected and placed in an appropriate container.
6. DNOC may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for dinitro-ortho-cresol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 2 mg/m^3	Any dust and mist respirator with a full facepiece
Less than or equal to 5 mg/m^3	Any powered air-purifying respirator with a dust and mist filter (substance causes eye irritation or damage—eye protection needed)
	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 5 mg/m^3	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.2 mg/m^3 (TWA).

Occupational Health Guideline for Dinitrotoluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 2,4-$(NO_2)_2C_6H_3CH_3$
- Synonyms: 2,4-Dinitrotoluene; DNT
- Appearance and odor: Orange-yellow solid (sometimes shipped molten in tank cars) with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dinitrotoluene is 1.5 milligrams of dinitrotoluene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dinitrotoluene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed; It is readily absorbed through the skin. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

1. Short-term Exposure: Dinitrotoluene affects the ability of blood to carry oxygen normally. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. The ingestion of alcohol may cause increased susceptibility to the effects of dinitrotoluene.

2. Long-term Exposure: Repeated or prolonged exposure to dinitrotoluene may cause anemia and jaundice.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dinitrotoluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dinitrotoluene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, liver, and cardiovascular system should be stressed.

—A complete blood count: Dinitrotoluene has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Observe for Heinz bodies.

—Liver function tests: Since liver damage has been observed in humans exposed to dinitrotoluene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur. The level of dinitrotoluene in the urine should be determined; excretion of dinitrotoluene in excess of 25 mg/liter indicates significant absorption.

- **Summary of toxicology**

Dinitrotoluene absorption, whether from inhalation of the vapor or absorption of the solid through skin, causes anoxia due to the formation of methemoglobin; jaundice and anemia have been reported. Signs and symptoms of

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overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious, and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is often recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual may feel well, have no complaints, and may insist that nothing is wrong until the methemoglobin concentrations approaches approximately 40%. At methemoglobin concentrations of over 40% there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol is reported to aggravate the toxic effects of dinitrotoluene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 182.1
2. Boiling point (760 mm Hg): Slow decompostion at 250 C (482 F); self-sustained decomposition at 270 C (518 F)
3. Specific gravity (water = 1): Solid: 1.52; Liquid: 1.32
4. Vapor density (air = 1 at boiling point of dinitrotoluene): Not applicable (too high boiling)
5. Melting point: 70 C (158 F)
6. Vapor pressure at 20 C (68 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 250 C (482 F)
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with caustics and chemically active metals such as tin or zinc may cause evolution of heat and increase in pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dinitrotoluene.
4. Special precautions: Liquid dinitrotoluene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 206.7 C (404 F) (closed cup)
2. Autoignition temperature: Data not available
3. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): Greater than 100 centimeters
4. Flammable limits in air, % by volume: Not available
5. Extinguishant: Water, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dinitrotoluene.
2. Eye Irritation Level: Grant states that "a severe burn of the skin, eyelids, and cornea of one eye, with permanent scarring, has been attributed in one instance to hot fumes of dinitrotoluene." There is no quantitative information available concerning the concentrations which would produce these effects.
3. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of dinitrotoluene to air concentration, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for dinitrotoluene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten dinitrotoluene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with dinitrotoluene or liquids containing dinitrotoluene, where skin contact may occur.
- If employees' clothing may have become contaminated with solid dinitrotoluene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with dinitrotoluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dinitrotoluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dinitrotoluene, the person performing the operation should be informed of dinitrotoluene's hazardous properties.
- Where exposure of an employee's body to dinitrotoluene or liquids containing dinitrotoluene may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes wet with molten dinitrotoluene or liquids containing dinitrotoluene should be removed immediately and non-impervious clothing which becomes contaminated with solid dinitrotoluene should be removed promptly and such clothing should not be reworn until the dinitrotoluene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten dinitrotoluene contacting the eyes.

SANITATION

- Skin that becomes wet with molten dinitrotoluene or liquids containing dinitrotoluene should be immediately washed or showered with soap or mild detergent and water to remove any dinitrotoluene.
- Workers subject to skin contact with dinitrotoluene or liquids containing dinitrotoluene should wash with soap or mild detergent and water any areas of the body which may have contacted dinitrotoluene at the end of each work day.
- Skin that becomes contaminated with dinitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any dinitrotoluene.
- Eating and smoking should not be permitted in areas where dinitrotoluene or liquids containing dinitrotoluene are handled, processed, or stored.
- Employees who handle dinitrotoluene or liquids containing dinitrotoluene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dinitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluene diisocyanate for production of polyurethane plastics	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of military and some commercial explosives; use to plasticize cellulose nitrate in explosives; use to moderate burning rate of propellants and explosives; use in manufacture of gelatin explosives (less sensitive to shock or friction); use as a water-proofing coating for some smokeless powders; use as an intermediate in TNT manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of azo dye intermediates; use in organic synthesis in preparation of toluidines, dyes, and explosives	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dinitrotoluene or liquids containing dinitrotoluene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. If molten dinitrotoluene gets into the eyes, flush the eyes immediately with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dinitrotoluene or liquids containing dinitrotoluene get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dinitrotoluene or liquids containing dinitrotoluene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately. If molten dinitrotoluene gets on the skin, immediately flush the skin with water to remove heat. Wash the skin with soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of dinitrotoluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dinitrotoluene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If dinitrotoluene is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other suitable material and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities may be reclaimed; however, if this is not practical, dissolve in fuel oil and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
4. If in the molten form, allow to cool and solidify and treat as in (3) above.

- Waste disposal methods:

Dinitrotoluene may be disposed of:

1. By making packages of dinitrotoluene in paper or other flammable material and burning in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device.
2. By dissolving dinitrotoluene in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DINITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 1.5 mg/m³
Particulate or Vapor Concentration	
15 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
75 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DI-2-ETHYLHEXYL PHTHALATE (DEHP)

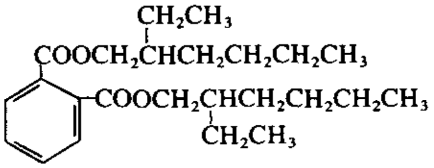
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about di-2-ethylhexyl phthalate (DEHP) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{24}H_{38}O_4$
- **Structure:**



- **Synonyms:** DEHP; 1,2-benzenedicarboxylic acid; bis(2-ethylhexyl) ester; bis(2-ethylhexyl) phthalate; DEHP; phthalic acid; bis(2-ethylhexyl) ester; di-sec octyl phthalate
- **Identifiers:** CAS 117-81-7; RTECS TI0350000; DOT not assigned
- **Appearance and odor:** Clear to slightly colored, oily, odorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 390.54
2. Boiling point (at 760 mmHg): 386°C (727°F)
3. Specific gravity (water = 1): 0.9861
4. Vapor density (air = 1 at boiling point of DEHP): 16
5. Melting point: -50°C (-58°F)
6. Vapor pressure: At 20°C (68°F), 0.01 mmHg; at 200°C (392°F), 1.32 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.005
8. Evaporation rate (butyl acetate = 1): Almost zero

- **Reactivity**

1. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, or strong acids may cause fire and explosion.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving DEHP.

- **Flammability**

1. Flash point: 218°C (425°F) (open cup)
2. Autoignition temperature: 390°C (735°F)
3. Flammable limits in air, % by volume: Lower, 0.3 at 245°C (474°F); Upper, Not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

- **Warning properties**

1. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DEHP is 5 milligrams of DEHP per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that DEHP be controlled and handled as a potential human carcinogen in the workplace, and the recommended exposure limit (REL) is that exposure be reduced to the lowest feasible limit. The use of DEHP in the quantitative fit testing of respirators should be discontinued and replaced with less toxic material such as refined corn oil. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 10 mg/m³ (Table 1).

Table 1.—Occupational exposure limits for di-2-ethylhexyl phthalate

	Exposure limits mg/m³
OSHA PEL TWA	5
NIOSH REL (Ca)*	Lowest feasible limit
ACGIH TLV® TWA	5
STEL	10

* (Ca): NIOSH recommends treating as a potential human carcinogen.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

DEHP may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Subchronic inhalation of DEHP by rats or mice caused pulmonary irritation, swelling, and congestion of the liver and kidneys, renal cysts, bladder stones, testicular degeneration, increased liver metabolism and liver and kidney weights, and reduced weight gain, renal concentration capacity, blood hematocrit, and cholesterol and triglyceride levels. Chronic inhalation of DEHP by mice or rats produced liver cancer. Oral administration of DEHP to mice or rats on various days during fetal development caused a reduction in implantation rates, an increase in embryolethality, delayed births, and malformations of the skeletal system and the external and central nervous systems. Two-generation reproduction studies in treated rats showed a depression in placental and fetal weights and an increase in liver and kidney weights.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to DEHP can cause gastric disturbances and diarrhea. Skin sensitization and irritation of the eyes, skin, and respiratory tract can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to DEHP, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, gastrointestinal tract, and reproductive and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DEHP. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver or skin. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DEHP. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, gastrointestinal tract, and reproductive and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and lung function tests.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DEHP may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting DEHP vapors with cellulose membrane filters followed by elution with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure DEHP may also be used if available. A detailed sampling and analytical method for DEHP may be found in the *NIOSH Manual of Analytical Methods* (method number 5020).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with DEHP.

SANITATION

Clothing which is contaminated with DEHP should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DEHP from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DEHP's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with DEHP should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DEHP should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DEHP may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for di-2-ethylhexyl phthalate (DEHP)

Operations	Controls
During bulk processing and application of plasticized polyvinyl chloride, polyvinylidene chloride, and other vinyl resins	Local exhaust ventilation, personal protective equipment
During hot processing of some plasticized polystyrenes, acrylics, urethanes, polyamides, and other synthetic resins	Local exhaust ventilation, personal protective equipment
During hot compounding plasticization of chlorinated rubbers and nitrile and neoprene rubbers	Local exhaust ventilation, personal protective equipment
During the application of nitrocellulose-based adhesives	Local exhaust ventilation, personal protective equipment
During hot esterification and subsequent steps in the manufacturing of DEHP	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DEHP, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DEHP gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to DEHP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DEHP gets on the skin, wash it immediately with soap and water. If DEHP penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DEHP is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing DEHP, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing DEHP may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing DEHP may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for di-2-ethylhexyl phthalate (DEHP)

Condition	Minimum respiratory protection*
Any detectable concentration	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Dioxane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $OCH_2CH_2OCH_2CH_2$
- Synonyms: Diethylene dioxide; diethylene ether; dioxan; p-dioxane; 1,4-dioxane
- Appearance and odor: Colorless liquid with a mild ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dioxane is 100 parts of dioxane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of dioxane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 1 ppm averaged over a 30-minute period, and that dioxane be regulated as an occupational carcinogen. The NIOSH Criteria Document for Dioxane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dioxane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Overexposure to dioxane may cause irritation of the eyes, nose, and throat. It may also cause drowsiness, dizziness, loss of appetite, headache, nausea, vomiting, stomach pain, and liver and kidney damage. Prolonged skin exposure to the liquid may cause drying and cracking. Dioxane has been shown to induce tumor formation in experimental animals.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dioxane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dioxane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the upper respiratory system, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Dioxane may cause liver damage. A profile of liver function should be performed by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Skin disease: Dioxane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—14" x 17" chest roentgenogram: Dioxane causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Dioxane is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Summary of toxicology**

Dioxane vapor is a mucous membrane irritant, and on prolonged exposure is toxic to the liver and kidneys. Repeated exposure of several animal species to 1000 ppm produced damage to kidneys and liver, and the repeated inhalation of 800 ppm over 30 days resulted in fatal kidney injury in some rabbits. Human volunteers exposed for 15 minutes to 300 ppm reported mild transient irritation of the eyes, nose, and throat. There is significant absorption of the liquid through the skin, adding to the inhalation hazard. Prolonged or repeated skin contact may also result in drying and cracking due to defatting action. Fatal intoxication due to liver necrosis and severe kidney damage has been reported in workers after two months of heavy exposure to dioxane vapor; the onset of poisoning was marked by drowsiness and headache, nausea, vomiting, and irritation of the eyes and respiratory passages. In one fatal case there was significant damage to the brain as well as to liver and kidney. Due to its mild odor, serious or fatal exposures have been experienced without forewarning. Tumors of the nose, liver, and lungs have been reported in animals following ingestion of high concentrations of dioxane. Immersion of chick embryoes in dioxane has been reported to cause possible mutagenic effects. The significance of these findings in humans in unknown.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 88
2. Boiling point (760 mm Hg): 101 C (214 F)
3. Specific gravity (water = 1): 1.03
4. Vapor density (air = 1 at boiling point of dioxane): 3.0
5. Melting point: 11.8 C (53 F)
6. Vapor pressure at 20 C (68 F): 29 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 2.7

- **Reactivity**

1. Conditions contributing to instability: Heat, long exposure to moisture.
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dioxane.
4. Special precautions: Dioxane is hydroscopic and will produce peroxides in the presence of moisture. Dioxane containing peroxides should not be distilled to dryness because of the potential explosion of non-volatile peroxides.

- **Flammability**

1. Flash point: 12 C (54 F) (closed cup)
2. Autoignition temperature: 180 C (356 F)
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 22.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Summer reports an odor threshold of 170 ppm; May reports 2.7 and 170 ppm.
2. Eye Irritation Level: Grant states that "in human beings, irritation of the eye is noted only at concentrations greater than 220 ppm of vapor in air." Patty states that at 300 ppm, dioxane "caused irritation of the eyes, nose, and throat; and at 500 ppm, it was objectionable. Even at higher concentrations, the initial irritation to eyes and respiratory passages is transitory . . . ."
3. Evaluation of Warning Properties: Patty states that the initial irritation produced by exposure to dioxane is transitory and that the "warning properties of dioxane are completely inadequate to prevent exposure to toxic amounts." The AIHA *Hygienic Guide* also notes that "the vapor has poor warning properties and can be inhaled in amounts which may cause serious intoxication or death with injury of the liver and kidneys."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dioxane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dioxane may be used. An analytical method for dioxane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted

are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid dioxane.
- Any clothing which becomes wet with liquid dioxane should be removed immediately and non-impervious clothing which becomes contaminated with dioxane should be removed promptly and such clothing should not be reworn until the dioxane is removed from the clothing.
- Clothing wet with liquid dioxane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dioxane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dioxane, the person performing the operation should be informed of dioxane's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dioxane may contact the eyes.

SANITATION

- Skin that becomes contaminated with dioxane should be promptly washed or showered to remove any dioxane.
- Eating and smoking should not be permitted in areas where liquid dioxane is handled, processed, or stored.
- Employees who handle liquid dioxane should wash their hands thoroughly before eating, smoking, or using toilet facilities.
- Areas in which exposure to dioxane may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dioxane may occur and control methods which may be effective in each case:

Operation	Controls
Use in spray application of natural and synthetic resin-based varnishes, lacquers, and paints	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in dipping, roller coating, tumbling, knifing, and brushing of natural and synthetic resin-based varnishes, lacquers, and paints	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for fats, oils, waxes, greases, and natural and synthetic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a wetting agent in textile processing, dye baths, and stain and printing compositions	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a degreaser	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a dehydrating agent in preparation of histological slides	Local exhaust ventilation
Use in manufacture of detergents and cleaning preparations; manufacture of polishing compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a stabilizer for chlorinated solvents; use in preparation of cosmetics and deodorants; use in purification of drugs	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a working fluid for scintillation counter samples	General dilution ventilation; personal protective equipment
Use as a solvent in pulping of wood; polishing compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dioxane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dioxane gets on the skin, promptly wash the contaminated skin with water. If dioxane soaks through the clothing, remove the clothing promptly and wash the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of dioxane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dioxane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dioxane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Dioxane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Dioxane may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*. Volume 11, 1976.

RESPIRATORY PROTECTION FOR DIOXANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
200 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 200 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Diphenyl*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5C_6H_5$ or $C_{12}H_{10}$
- Synonyms: Biphenyl; phenylbenzene
- Appearance and odor: Colorless to pale yellow solid with a very characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diphenyl is 0.2 part of diphenyl per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1 milligram of diphenyl per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diphenyl can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin. (It may be absorbed through the skin).

- **Effects of overexposure**

1. Short-term Exposure: Exposure to diphenyl may cause irritation of the eyes and throat.

2. Long-term Exposure: Repeated exposure to diphenyl may cause headache, nausea, indigestion, abdominal pain, fatigue, numbness, and aching of the limbs (nervous system damage), and liver damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diphenyl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diphenyl at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from diphenyl exposure.

—Liver disease: Exposure to high concentrations of vapor may incur damage to the liver, to which individuals with pre-existing liver disease may be more susceptible.

—Skin disease: Diphenyl can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Central nervous system disorders: Exposure to high concentrations of vapor may cause damage to the central nervous system, to which individuals with pre-existing conditions may be more susceptible.

—Kidney disease: Although diphenyl is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

At concentrations of 5 mg/m^3 or higher, irritation of the eyes and throat has been reported. Employees with repeated exposure to higher concentrations had gastrointestinal symptoms as well as polyneuritic complaints, with abnormalities of both the electroencephalogram and the electromyogram. Some showed hepatic damage detected by liver function tests and biopsy, and one fatal case of liver necrosis with some areas of cirrhosis occurred in an individual who had been exposed regularly to concentrations of vapor in air of approximately 100 mg/m^3. At higher concentrations, mice and rats

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showed damage to the liver and kidney, as well as broncho-pulmonary effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 154
2. Boiling point (760 mm Hg): 254 C (489 F)
3. Specific gravity (water = 1): 1.04
4. Vapor density (air = 1 at boiling point of diphenyl): Not applicable
5. Melting point: 69 C (156 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving diphenyl.
4. Special precautions: None

- **Flammability**

1. Flash point: 113 C (235 F) (closed cup)
2. Autoignition temperature: 538 C (1004 F)
3. Flammable limits in air, % by volume: Lower: 0.6 at 111 C (212 F); Upper: 5.8 at 155 C (311 F)
4. Extinguishant: Water. dry chemical, carbon dioxide, and foam.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that diphenyl has a "distinctive aromatic odor" which is detectable at 0.06 to 0.29 mg/m³.
2. Eye Irritation Level: Concerning eye irritation, the *Hygienic Guide* reports that "mild to moderate irritation is reported by humans exposed to the vapor." Grant reports that when concentrations of 3 to 4 ppm of Dowtherm A (a mixture of diphenyloxide (75%) and diphenyl (25%)) are reached, there is irritation of the eyes, nose, and throat."
3. Evaluation of Warning Properties: Since the odor threshold of diphenyl is well below the permissible exposure limit, diphenyl is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for diphenyl is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid diphenyl or liquids containing diphenyl.
- If employees' clothing may have become contaminated with solid diphenyl, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with diphenyl should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diphenyl from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diphenyl, the person performing the operation should be informed of diphenyl's hazardous properties.
- Non-impervious clothing which becomes contaminated with diphenyl should be removed promptly and not reworn until the diphenyl is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of molten diphenyl contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid diphenyl or liquids containing diphenyl may contact the eyes.

SANITATION

- Skin that becomes contaminated with solid diphenyl or liquids containing diphenyl should be promptly washed or showered with soap or mild detergent and water to remove any diphenyl.
- Eating and smoking should not be permitted in areas where solid diphenyl or liquids containing diphenyl are handled, processed, or stored.
- Employees who handle solid diphenyl or liquids containing diphenyl should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diphenyl may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mixing for paper impregnation process	Local exhaust ventilation; personal protective equipment
Liberation during impregnation process for producing wrapping papers	Local exhaust ventilation
Liberation during wrapping and packaging of citrus with diphenyl-impregnated paper	Local exhaust ventilation; personal protective equipment
Liberation during use as a dye carrier for plastics and synthetic resin dyeing; during production of derivatives as diphenyl oxide	General dilution ventilation
Use as a heat-transfer medium	General dilution ventilation; personal protective equipment
Liberation during solvent applications in producing allyl alcohol from propylene oxide or phenol	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If diphenyl gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If diphenyl gets on the skin, immediately flush the contaminated skin with water. If diphenyl soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of diphenyl, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If diphenyl has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If diphenyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, use a procedure similar to that for small quantities.

- Waste disposal methods:

Diphenyl may be disposed of:

1. By making packages of diphenyl in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving diphenyl in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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* SPECIAL NOTE

Diphenyl appears on the Environmental Protection Agency's (EPA) Chemical Assessment Group "List of Chemicals" having substantial evidence of carcinogenicity (Environmental Protection Agency, Washington, D.C., 22 April 1980).

RESPIRATORY PROTECTION FOR DIPHENYL

Condition	Minimum Respiratory Protection* Required Above 1 mg/m^3 (0.2 ppm)
Particulate or Vapor Concentration	
10 mg/m^3 (2 ppm) or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s). Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m^3 (10 ppm) or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
300 mg/m^3 (60 ppm) or less	A powered air-purifying chemical cartridge respirator with a full facepiece, organic vapor cartridge, and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 300 mg/m^3 (60 ppm) or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dipropylene Glycol Methyl Ether

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH(OCH_3)CH_2OCH_2CH(OH)CH_3$
- Synonyms: Dipropylene glycol monomethyl ether; Dowanol 50B
- Appearance and odor: Colorless liquid with a weak odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dipropylene glycol methyl ether is 100 parts of dipropylene glycol methyl ether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 600 milligrams of dipropylene glycol methyl ether per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dipropylene glycol methyl ether can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to high airborne levels or liquid splashes of dipropylene glycol methyl ether may cause irritation of the eyes and nose. Swallowing, breathing, or absorbing this chemical through the skin may cause nausea and sleepiness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dipropylene glycol methyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dipropylene glycol methyl ether at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from dipropylene glycol methyl ether exposure.

—Liver disease: Although dipropylene glycol methyl ether is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although dipropylene glycol methyl ether is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of dipropylene glycol methyl ether might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Dipropylene glycol methyl ether is primarily a narcotic with mild irritating properties. Single 7-hour exposures of rats to 500-ppm vapor resulted in only mild narcosis with rapid recovery. Repeated daily inhalation exposures to four animal species at 300 to 400 ppm also produced mild narcosis but no other significant effects. These levels are disagreeable to humans, causing some eye and nasal irritation. High vapor concentrations or liquid splashes cause transient irritation of the eyes. There is no skin irritation from even prolonged or

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repeated contact. Chronic systemic effects have not been observed in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 148
2. Boiling point (760 mm Hg): 190 C (374 F)
3. Specific gravity (water = 1): 0.95
4. Vapor density (air = 1 at boiling point of dipropylene glycol methyl ether): 5.11
5. Melting point: −83 C (−117 F)
6. Vapor pressure at 20 C (68 F): 0.3 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 0.02

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dipropylene glycol methyl ether.
4. Special precautions: Dipropylene glycol methyl ether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 85 C (185 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Browning states that dipropylene glycol monomethyl ether has "a mild ether odor in moderate concentrations but a strong objectionable odor at 1000 ppm."
2. Eye Irritation Level: Dipropylene glycol methyl ether vapor is not known to be an eye irritant, but, according to Patty, the undiluted liquid when placed in a rabbit's eye "on each of five consecutive days (causes) a mild transitory irritation of the conjunctival membranes."
3. Other Information: According to Browning, "high concentrations of the vapor cause marked irritation of the nasal mucuous membrane, which is difficult for humans to tolerate."
4. Evaluation of Warning Properties: Browning reports that nasal irritation is a warning property which "is a valuable protection against concentrations which might have toxic effects, and an inhalation hazard is not likely since, as Rowe remarks, 'levels that may be toxic on repeated exposure probably will not be tolerated voluntarily.'" The *Documentation of TLV's* notes that concentrations of 300 to 400 ppm "were very disagreeable to man; levels of 100 ppm, which might be voluntarily tolerated without complaints, were considered to be safe with respect to organic injury."

For the purposes of this guideline, dipropylene glycol methyl ether is treated as a material with good warning properties.

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dipropylene glycol methyl ether vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dipropylene glycol methyl ether may be used. An analytical method for dipropylene glycol methyl ether is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Clothing wet with liquid dipropylene glycol methyl ether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dipropylene glycol methyl ether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dipropylene glycol methyl ether, the person performing the operation should be informed of dipropylene glycol methyl ether's hazardous properties.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dipropylene glycol methyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a general solvent for oils and greases; use in application of coating materials	General dilution ventilation
Use as a coupling and dispersing agent in manufacture and application of printing pastes, dyes, and inks	General dilution ventilation
Use in manufacture of cosmetics	General dilution ventilation
Use in manufacture of latex paints, lacquers, and leather protective coatings	General dilution ventilation
Use as a slimicide in food packaging and adhesives in food industry	General dilution ventilation
Use as a heat-transfer agent in hydraulic brake fluid	General dilution ventilation
Use in glass cleaning, metal cleaning, and antifogging compositions	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If dipropylene glycol methyl ether gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dipropylene glycol methyl ether saturates the clothing, promptly remove the clothing and wash or shower. Wash any dipropylene glycol methyl ether from the skin regularly. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of dipropylene glycol methyl ether, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When dipropylene glycol methyl ether has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If dipropylene glycol methyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber or absorbed in vermiculite, dry sand, earth, or a similar material and disposed of in a sanitary landfill.

- Waste disposal methods:

Dipropylene glycol methyl ether may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a sanitary landfill.
2. By atomizing in a suitable combustion chamber.

- American Conference of Governmental Industrial Hygienists: "Dipropylene Glycol Methyl Ether," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
- Dow Chemical Company: *Material Safety Data Sheet – Dipropylene Glycol Methyl Ether.*

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Rowe, V. K., et al.: "Toxicology of Mono-, Di-, and Tri- Propylene Glycol Methyl Ethers," *A.M.A. Archives of Industrial Hygiene and Occupational Medicine*, 9:509-525, 1954.

RESPIRATORY PROTECTION FOR DIPROPYLENE GLYCOL METHYL ETHER

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIPROPYL KETONE

INTRODUCTION

This guideline summarizes pertinent information about dipropyl ketone for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{14}O$

- **Structure**

$(CH_3CH_2CH_2)_2CO$

- **Synonyms**

4-Heptanone; DPK; butyrone; GBL; Heptan-4-one; propyl ketone

- **Identifiers**

1. CAS No.: 123-19-3
2. RTECS No.: MJ5600000
3. DOT UN: 2710 26
4. DOT label: Flammable liquid

- **Appearance and odor**

Dipropyl ketone is a combustible, colorless liquid with a pleasant but penetrating odor and a burning taste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.2
2. Boiling point (760 mm Hg): 144°C (291°F)
3. Specific gravity (water = 1): 0.82 at 15°C (59°F)
4. Vapor density (air = 1 at boiling point of dipropyl ketone): 3.9
5. Melting point: -32.6°C (-26.7°F)
6. Vapor pressure at 20°C (68°F): 5.2 mm Hg
7. Solubility: Insoluble in water; miscible with alcohol and ether.
8. Evaporation rate: Data not available.

- **Reactivity**

1. Conditions contributing to instability: Heat and open flame
2. Incompatibilities: Contact of dipropyl ketone with oxidizing agents may cause a violent reaction.

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3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving dipropyl ketone.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to dipropyl ketone.

1. Flash point: 49°C (120°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol-resistant foam to fight fires involving dipropyl ketone. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving dipropyl ketone should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of dipropyl ketone may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dipropyl ketone. Structural firefighters' protective clothing may provide limited protection against fires involving dipropyl ketone.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dipropyl ketone [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (235 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for dipropyl ketone [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dipropyl ketone a threshold limit value (TLV) of 50 ppm (233 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on mild toxicity and liver effects in animals caused by exposure to high concentrations of dipropyl ketone [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dipropyl ketone can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dipropyl ketone is a mild irritant of the eyes and skin and, at high concentrations, a narcotic in animals. Applied to the eyes of rabbits, dipropyl ketone produced mild irritation [NIOSH 1994]. A single application of this substance to the skin of guinea pigs caused slight irritation, but repeated applications of 0.5 ml over a 10-day period caused more serious inflammation [Clayton and Clayton 1982]. In rabbits, the dermal LD_{50} is 5,660 mg/kg [NIOSH 1994]. Fifty percent of rats inhaling a 2,690-ppm concentration of dipropyl ketone for 6 hours (LC_{50}) died; before death, these animals exhibited somnolence and respiratory depression [NIOSH 1994; Clayton and Clayton 1982]. Rats exposed to a dipropyl ketone concentration of 400 ppm for 6 hours showed signs of respiratory depression, and those exposed to 1,600 ppm for the same period became

narcotic [Clayton and Clayton 1982]. The oral LD_{50} in rats is 3,730 mg/kg [NIOSH 1994]. Rats exposed for 6 hours/day, 5 days/week for 2 weeks to a 1,200-ppm dipropyl ketone atmosphere had slightly enlarged livers, although no changes in hematology or serum chemistry were seen [Clayton and Clayton 1982]. Rats gavaged with 2,000 mg/kg dipropyl ketone for 5 days/week for 12 weeks showed signs of severe central nervous system depression and had a reduced rate of weight gain; when the dose was lowered to 1,000 mg/kg, weight gain improved and no clinical abnormalities were seen. At autopsy, however, animals in both dose groups had increased liver and kidney weights and showed hepatocyte hypertrophy [Clayton and Clayton 1982].

2. *Effects on Humans:* Contact of the skin or eyes with the liquid or vapor causes skin or eye irritation [Clayton and Clayton 1982]. Based on effects seen in animals, acute exposure to dipropyl ketone may cause central nervous system depression in humans, and chronic exposure could lead to liver damage [Clayton and Clayton 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dipropyl ketone include redness and inflammation of the eyes and eyelids, coughing and sneezing, and redness and inflammation of the skin. At higher concentrations, dizziness, sleepiness, slowed breathing, and unconsciousness may occur.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dipropyl ketone may include enlargement of the liver, with jaundice and elevated liver enzymes, and kidney damage, with elevated urinary protein or creatinine levels and blood or pus in the urine. Dryness and cracking of the skin may occur on prolonged or repeated contact.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dipropyl ketone. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dipropyl ketone or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dipropyl ketone and lead to worker exposures to this substance:

—Use as a solvent for nitrocellulose, raw and blown oils, resins, and polymers

—Use in food flavorings and in lacquer formulations

The following methods are effective in controlling worker exposures to dipropyl ketone, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to dipropyl ketone, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, mucous membranes, skin, and central nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dipropyl ketone at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, mucous membranes, skin, or central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dipropyl ketone exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dipropyl ketone on the eyes, mucous membranes, skin, and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dipropyl ketone.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dipropyl ketone is made using a Carbosieve S-III tube (130/65 mg sections; 60/80 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 3 liters is collected. The sample is then treated with a carbon disulfide/dimethylformamide mixture (99:1) to extract the dipropyl ketone. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If dipropyl ketone contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dipropyl ketone should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dipropyl ketone, particularly its potential to cause skin irritation.

A worker who handles dipropyl ketone should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dipropyl ketone or a solution containing dipropyl ketone is handled, processed, or stored.

STORAGE

Dipropyl ketone should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of dipropyl ketone should be protected from physical damage and should be stored separately from oxidizing agents, reducing agents, bases, heat, sparks, and open flame. Only nonsparking tools may be used to handle dipropyl ketone. Because containers that formerly contained dipropyl ketone may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dipropyl ketone, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the dipropyl ketone for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Dipropyl ketone is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dipropyl ketone; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dipropyl ketone emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dipropyl ketone is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dipropyl ketone exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with dipropyl ketone. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dipropyl ketone permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dipropyl ketone.

If dipropyl ketone is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dipropyl ketone might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dipropyl ketone. Contact lenses should not be worn if the potential exists for dipropyl ketone exposure.

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Clayton G, Clayton F [1982]. Patty's industrial hygiene and toxicology. 3rd rev. ed. New York, NY: John Wiley & Sons.

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NIOSH [1992]. NIOSH recommendation for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

NIOSH [1994]. Registry of toxic effects of chemical substances databases: dipropyl ketone. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

OSHA [1989]. OSHA Laboratory In-House Methods File. Salt Lake City, UT: U.S. Department of Labor, OSHA Analytical Laboratory, P. O. Box 65200, 1781 South 300 West, Salt Lake City, Utah 84165-0200.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DISULFIRAM

INTRODUCTION

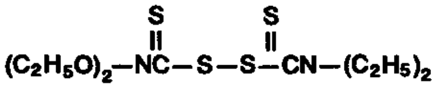
This guideline summarizes pertinent information about disulfiram for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{20}N_2S_4$

- **Structure**



$(C_2H_5O)_2{-}N\overset{\overset{S}{\|}}{C}{-}S{-}S{-}\overset{\overset{S}{\|}}{C}N{-}(C_2H_5)_2$

- **Synonyms**

Antabuse; bis(diethylthiocarbamoyl)disulfide; Abstensil; Alcophobin; Antethyl; Aversan; bis((diethylamino)thioxomethyl)disulphide; Disulfan; ethyl thiurad; Thiosan; tetraethylthiram disulfide; tetraethylthiuram disulfide; TTD

- **Identifiers**

1. CAS No.: 97-77-8
2. RTECS No.: JO1225000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Disulfiram is a yellow-white crystalline solid or gray powder that has a slight odor and a slightly bitter taste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 296.54
2. Boiling point (17 mm Hg): 117°C (242.6°F)
3. Specific gravity (water = 1): 1.3 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 70°C (158°F)
6. Vapor pressure: Data not available
7. Solubility: Insoluble in water; soluble in acetone, benzene, chloroform, carbon disulfide, ether, and alcohol; slightly soluble in light petroleum.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: None reported
3. Hazardous decomposition products: Toxic gases (such

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as carbon dioxide, nitrogen dioxide, and sulfur dioxide) may be released in a fire involving disulfiram.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to disulfiram.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving disulfiram should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of disulfiram should be moved from the fire area if it is possible to do so safely. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving disulfiram.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for disulfiram [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned disulfiram a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cytochrome P450 inhibition, d-amino acid inhibition, and aldehyde dehydrogenase inhibition associated with disulfiram exposure [NIOSH 1992]. The ACGIH limit is based on the risk of vasodilation, tachycardia, nausea, and hypotension associated with concomitant exposure to disulfiram and alcohol [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to disulfiram can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to disulfiram produces irritation and central nervous system effects in experimental animals. The oral LD_{50} is 500 mg/kg in rats, 1,980 mg/kg in mice, and 2,050 mg/kg in rabbits [NIOSH 1993]. The major signs of acute toxicity are ataxia, hypothermia, and paralysis [IARC 1976]. A disulfiram solution with a pH of 5.1 caused reversible and slight irritation and corneal opacity when instilled into rabbit eyes [NLM 1993]. In chronic exposure studies, rats fed disulfiram at doses of 1,000 to 2,000 mg/kg/day showed growth retardation, decreased reproductive capacity, and decreased life span [IARC 1976]. In rats exposed to disulfiram at a dose of 100 mg/kg/day from day 3 of gestation, increased fetal resorptions were seen but no teratogenic effects were observed in the surviving offspring [NLM 1993].

2. *Effects on Humans:* The human toxicology of disulfiram may be divided into those effects related to disulfiram alone and those effects associated with the combination of disulfiram and alcohol. Disulfiram alone may produce toxic effects on the nervous system, thyroid, and skin. The combination of disulfiram and alcohol causes a toxic syndrome related to elevated acetaldehyde levels (called the "Antabuse reaction"). The lowest oral dose of disulfiram reported to be lethal in an adult male is 160 mg/kg [NIOSH 1993]. Studies have shown that a small dose of disulfiram can cause a measurable effect on thyroid iodine uptake and also can cause thyroid gland hypertrophy

[Hayes 1982]. Disulfiram can also produce acneform skin rashes, dermatitis, and urticaria [Gilman et al. 1985]. Exposure to disulfiram and concomitant ingestion of alcohol produces a syndrome that begins with a sensation of heat, facial flushing, restlessness, and anxiety and progresses to palpitations, increased heart and respiratory rates, hypotension, chest pain, sweating, nausea, vomiting, weakness, dizziness, and confusion. Atypical and severe reactions have included convulsions, cardiac arrhythmias, myocardial infarction, marked respiratory depression, and acute congestive heart failure [Gosselin et al. 1984]. This syndrome has occurred in workers who have ingested alcohol and then been exposed to disulfiram, as well as to patients exposed to disulfiram as a medication [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to disulfiram may cause headaches, drowsiness, fatigue, dizziness, impaired sexual functioning, a garlic or metallic taste in the mouth, mild gastrointestinal symptoms, depression, psychosis, and confusion. The signs and symptoms of disulfiram-induced peripheral neuropathy may include visual impairment, muscle weakness, numbness, and tingling, and skin reactions to disulfiram exposure may include acneform eruptions, redness, swelling, scaling, and itching.

2. *Chronic exposure:* Chronic exposure to disulfiram may cause identical signs and symptoms to those associated with acute exposure.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if disulfiram or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve disulfiram and lead to worker exposures to this substance:

—Use as a rubber accelerator and vulcanizer

—Use as a medication in the treatment of alcoholism

—Use as a seed disinfectant and fungicide

The following methods are effective in controlling worker exposures to disulfiram, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to disulfiram, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on a history of skin allergies and excessive alcohol intake and on the function and integrity of the central and peripheral nervous systems, eyes, skin, liver, and thyroid.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to disulfiram at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with excessive alcohol intake or with diseases of the eyes, skin, nervous system, liver, or thyroid.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to disulfiram exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of disulfiram on the eyes, skin, nervous system, liver, or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Disulfiram and its metabolites can be detected in the blood, urine, and breath of exposed individuals. However, no method of correlating airborne concentrations of disulfiram with concentrations in the blood, urine, or breath has been developed. Therefore, no biological monitoring test acceptable for routine use has yet been developed for disulfiram.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne disulfiram is made using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Samples are extracted with methanol, and analysis is conducted by high-performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If disulfiram contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with disulfiram should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles disulfiram should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where disulfiram or a solution containing disulfiram is handled, processed, or stored.

STORAGE

Disulfiram should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of disulfiram should be protected from physical damage and should be stored separately from phenols, flammable substances, heat, sparks, and open flame. Because containers that formerly contained disulfiram may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving disulfiram, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate the area of the spill or leak.
4. Collect powdered material in the most convenient manner and deposit in sealed containers.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Disulfiram is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of disulfiram; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of disulfiram emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although disulfiram is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of disulfiram exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with disulfiram. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to disulfiram permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to disulfiram.

If disulfiram is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which disulfiram might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with disulfiram. Contact lenses should not be worn if the potential exists for disulfiram exposure.

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OSHA [1992]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIURON

INTRODUCTION

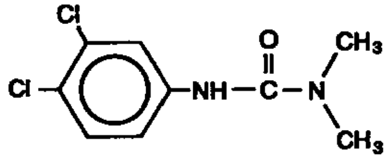
This guideline summarizes pertinent information about diuron for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{10}Cl_2N_2O$

- **Structure**



- **Synonyms**

3-(3,4-Dichlorophenyl)-1,1-dimethylurea; dichlorfenidim; Crisuron; Diurex; Karmex Diuron Herbicide; Telvar Diuron Weed Killer

- **Identifiers**

1. CAS No.: 330-54-1
2. RTECS No.: YS8925000
3. DOT UN: 2767 55
4. DOT label: None

- **Appearance and odor**

Diuron is a white, odorless, crystalline solid. It is available commercially as an 80 percent wettable powder or a 35 percent aqueous suspension.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 233.1
2. Boiling point (760 mm Hg): 189° to 190°C (372.2° to 374°F) (decomposes)
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: 158° to 159°C (316.4° to 318.2°F)
6. Vapor pressure at 50°C (122°F): 0.0000031 mm Hg

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7. Solubility: Slightly soluble in water and hydrocarbons; soluble in acetone.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving diuron.

4. Special precautions: Diuron hydrolyzes in fairly strong acids.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating for diuron; this substance is not flammable.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, CO_2, water spray, fog, or standard foam to fight fires involving diuron.

Fires involving diuron should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of diuron should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diuron. Chemical protective clothing that is specifically recommended for diuron may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving diuron.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diuron [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for diuron [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diuron a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation associated with diuron exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diuron can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Acute exposure to diuron causes mild skin irritation and narcosis in animals, and chronic exposure to this substance may cause blood changes and spleen and liver enlargement. In contact with the unbroken skin of guinea pigs, diuron caused no irritation; in contact with broken skin, however, this substance caused a moderate degree of irritation [EPA 1987]. The dermal LD_{50} in rabbits is greater than 2,500 mg/kg [EPA 1987]. Instilled into the eyes of rabbits, diuron caused no irritation [EPA 1987]. The oral LD_{50} in rats is 1,017 mg/kg [NIOSH 1993]. Acutely poisoned animals showed signs of central

nervous system depression before death [EPA 1987]. Rats fed daily doses of diuron ranging from 2,000 to 8,000 ppm in the diet for 42 days showed decreased red blood cell counts and hemoglobin values (2,000 ppm or greater), growth retardation (4,000 ppm or greater), and increased mortality (8,000 ppm) [EPA 1987]. Rats fed diuron at a dietary dose of 5,000 ppm for 90 days showed reduced body weights, enlarged spleens, splenic hemosiderosis, and chronic methemoglobinemia [EPA 1987]. Rats fed diuron at a dietary dose of 250 ppm or higher for 2 years showed growth retardation, decreased red blood cell counts, decreased hemoglobin values, splenic hemosiderosis, and increased mortality [EPA 1987]. Oral exposure to 250 mg/kg/day of an 80 percent diuron solution on days 6 through 15 of gestation caused a statistically significant increase in wavy rib abnormalities in the offspring of rats [EPA 1987].

2. *Effects on Humans:* No information on the toxic effects of occupational exposure to diuron is available. Based on effects seen in animals, acute exposure to diuron would be expected to cause mild skin irritation and headaches, drowsiness, and incoordination in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to diuron have been reported in humans.
2. *Chronic exposure:* No signs or symptoms of chronic exposure to diuron have been reported in humans.

- **Emergency procedures**

> WARNING!
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diuron or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diuron and lead to worker exposures to this substance:

—Manufacture, formulation, and use as a pre-emergence herbicide

—Use as a general weed killer and as a soil sterilant

—Use as a sugar cane flowering suppressant

The following methods are effective in controlling worker exposures to diuron, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to diuron, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diuron at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with adverse effects on the blood.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diuron exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diuron on the blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for diuron.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne diuron is made using an OSHA Versatile Sampler (OVS-2) 13 mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If diuron contacts the skin, workers should wash the affected areas immediately with soap and water.

Clothing contaminated with diuron should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles diuron should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diuron or a solution containing diuron is handled, processed, or stored.

STORAGE

Diuron should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diuron should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained diuron may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diuron, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Water spray may be used to reduce vapors.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the diuron for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

Emergency planning requirements

Diuron is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

Reportable quantity requirements for hazardous releases

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for diuron is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employees are required to do the following:

—Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diuron emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diuron is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diuron exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, and coveralls, as appropriate) should be worn to prevent skin contact with diuron. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to diuron permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diuron.

If diuron is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diuron might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diuron. Contact lenses should not be worn if the potential exists for diuron exposure.

REFERENCES CITED

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ENDOSULFAN

INTRODUCTION

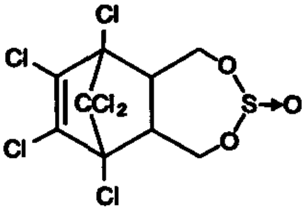
This guideline summarizes pertinent information about endosulfan for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_6Cl_6O_3S$

- **Structure**



- **Synonyms**

6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide; Benzoepin; Beosit; Chlorthiepin; Crisulfan; Cyclodan; Devisulphan; Endocel; Endosol; Ensure; Hildan; Insectophene; Kop-Thiodan; Malix; Niagara 5,462; Thiodan; Thifor; Thiosulfan; Tiovel

- **Identifiers**

1. CAS No.: 115-29-7
2. RTECS No.: RB9275000
3. DOT NA: 2761 55
4. DOT label: Poison

- **Appearance and odor**

Endosulfan is a tan, semi-waxy solid that is a mixture of two isomers; it may have a slight, sulfur dioxide-like odor. This substance is an organochlorine pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 406.95
2. Boiling point: 106°C (222.8°F) at 0.7 mm Hg
3. Specific gravity (water = 1): 1.75 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 108° to 110°C (226.4° to 230°F) alpha isomer; 208° to 210°C (406.4° to 410°F) beta isomer; 70° to 100°C (158° to 212°F) mixture
6. Vapor pressure at 25°C (77°F): 0.00001 mm Hg
7. Solubility: Insoluble in water; moderately soluble in most organic solvents; soluble in xylene, kerosene, chloroform, acetone, and alcohol.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, open flame, moisture, and air.
2. Incompatibilities: Edosulfan is incompatible with acids and alkalies (which can cause it to hydrolyze) and is corrosive to iron.
3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of sulfur) may be released in a fire involving endosulfan.
4. Special precautions: None reported

Flammability

The National Fire Protection Association had not assigned a fire hazard rating for endosulfan; this substance may burn, but it does not ignite readily.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use dry chemical, carbon dioxide, water spray, standard foam, or fog to fight fires involving endosulfan. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving endosulfan should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of endosulfan may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving endosulfan. Chemical protective clothing that is specifically recommended for endosulfan may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving endosulfan.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for endosulfan [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for endosulfan. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned endosulfan a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to endosulfan [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of convulsions associated with endosulfan exposure and the high toxicity in experimental female animals caused by endulsofan exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to endosulfan can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Endosulfan causes central nervous system, kidney, liver, and testicular effects in animals. The dermal LD$_{50}$ in rabbits is 90 mg/kg [NIOSH 1993]. The 4-hr LC$_{50}$ is 80 mg/m^3 in rats [NIOSH 1993]. The oral LD$_{50}$ is 18 mg/kg in rats and 7.4 mg/kg in mice [NIOSH 1993]. Farm animals ingesting endosulfan (dose not specified) exhibited ataxia and seizures [Hayes 1982]. Some rats given

oral doses (10 mg/kg/day) died after 15 days; at 5 mg/kg/day, rats survived but showed signs of liver damage at autopsy [Hayes 1982]. In one oral feeding study, rats tolerated endosulfan doses of 2.5 mg/kg/day for 24 months without effects, but feeding at a dose of 5 mg/kg/day for the same period reduced the growth and survival rates in female rats, caused changes in the kidneys of male rats, and caused blood changes in rats of both sexes [ACGIH 1991]. Oral doses of 10 mg/kg/day for 15 days caused degeneration of the somniferous tubules and a significant decrease in testis weight among male rats [ACGIH 1991]. A dose of 5 mg/kg/day or higher on gestation days 6 through 14 increased the mortality of rat dams and increased the rates of resorption and skeletal abnormalities in their offspring [ACGIH 1991].

2. *Effects on Humans:* Endosulfan causes central nervous system and respiratory effects in humans. The estimated lethal dose of endosulfan in humans is 50 to 500 mg/kg [Gosselin et al. 1984]. Suicides and accidental deaths have been described after acute exposure to endosulfan; these episodes resulted in gagging, vomiting, diarrhea, agitation, convulsions, foaming at the mouth, difficulty breathing, apnea, cyanosis, and loss of consciousness [Hayes 1982]. One or more seizures occurred in nine workers exposed to endosulfan while performing various tasks, including the bagging of a 50 percent water-wettable endosulfan powder. These workers experienced a prodromal syndrome consisting of malaise, nausea, vomiting, dizziness, weakness, confusion, and headache. Recovery occurred within a few days [ACGIH 1991; Hayes 1982]. In a case involving subchronic exposure, a worker cleaning vats that contained endosulfan residues developed malaise, fainting spells, and seizures; after 4 months of exposure, this worker had three consecutive seizures that resolved after emergency medical treatment. Later, gross cognitive deficits and agitation were diagnosed; 2 years later, this worker continued to have memory impairment, nominal aphasia, and poor visual-motor coordination [Aleksandrowicz 1979].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute oral exposure to endosulfan include malaise, nausea, vomiting, dizziness, weakness, confusion, headache, nervousness, agitation, tremor, seizures, convulsions, diarrhea, difficult breathing, cyanosis, and loss of consciousness. Inhalation exposure may cause nausea, confusion, excitement, flushing, and dry mouth.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to endosulfan include malaise, fainting, seizures, convulsions, agitation, cognitive impairments, and respiratory impairment (including shortness of breath and cough).

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure: **Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Endosulfan can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if endosulfan or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

- —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do *not* give syrup of ipecac because of possible onset of respiratory depression and seizures.

- —Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve endosulfan and lead to worker exposures to this substance:

—Use as an insecticide for deciduous fruits, nuts, cotton and vegetables, ornamentals, tea, and coffee

—Use as an acaricide against aphids, thrips, beetles, foliar feeding larvae, cutworms, leafhoppers, the tsetse fly, and slugs

The following methods are effective in controlling worker exposures to endosulfan, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to endosulfan, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

  A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to endosulfan at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to endosulfan exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of endosulfan on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for endosulfan.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne endosulfan is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) and an enclosed glass fiber filter. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 60 liters is collected. Analysis is conducted by gas chromatography using an electron capture detector. This method is described in the OSHA Computerized Information System [OSHA 1993].

PERSONAL HYGIENE

Endosulfan can be absorbed through the skin in toxic amounts. Therefore, if endosulfan contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with endosulfan should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of endosulfan, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles endosulfan should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where endosulfan or a solution containing endosulfan is handled, processed, or stored.

STORAGE

Endosulfan should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of endosulfan should be protected from physical damage and should be stored separately from alkalies, acids, heat, sparks, and open flame. Because containers that formerly contained endosulfan may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving endosulfan, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into of the spill to contain the endosulfan for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  The owners and operators of a facility must comply with EPA's emergency planning requirements if 1 lb or more of endosulfan is present at the facility.

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for endosulfan is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of endosulfan emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Endosulfan is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P050. Endosulfan is approved for land disposal as long as the concentration of endosulfan in the waste or treatment residual does not exceed 0.13 mg/kg. Endosulfan also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of endosulfan exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with endosulfan. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. One source recommends the use of protective gloves and clothing made of Viton or neoprene for protection against permeation by endosulfan.

If endosulfan is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which endosulfan might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with endosulfan. Contact lenses should not be worn if the potential exists for endosulfan exposure.

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Occupational Health Guideline for Endrin

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_{8}Cl_{6}O$
- Synonyms: 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene
- Appearance and odor: Colorless to tan solid with a mild chemical odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for endrin is 0.1 milligram of endrin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Endrin can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to endrin may cause sudden convulsions which may occur from 30 minutes to 10 hours after exposure. Headache, dizziness, sleepiness, weakness, and loss of appetite may be present for two to four weeks following this exposure. A number of deaths have occurred from swallowing endrin. In less severe cases of endrin poisoning, the complaints include headache, dizziness, abdominal discomfort, nausea, vomiting, insomnia, agitation, and mental confusion. Experimental feeding of endrin to animals has produced abnormalities in their offspring.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to endrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to endrin at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders would be expected to be at increased risk from exposure. Examination of the nervous system and liver should be stressed. The concentration of endrin in the blood is helpful in determining the extent of absorption.

2. Periodic Medical Examination: The aforementioned medical examination should be repeated on an annual basis.

- **Summary of toxicology**

Endrin as the dust or in solution is a convulsant. Single doses of 2.5 mg/kg of endrin administered orally to pregnant golden hamsters during the period of fetal organogenesis caused a high incidence of fetal deaths, congenital anomalies, and growth retardation. Rats fed a diet of 50 or 100 ppm endrin for 2 years developed degenerative changes in the liver. In humans, the first effect of endrin intoxication is frequently a sudden epileptiform convulsion, which may occur from 30 minutes to up to 10 hours after overexposure; it lasts for several minutes and is usually followed by a stuporous state for 15 minutes to 1 hour. The electroencephalogram may show dysrhythmic changes which frequently precede convulsions; withdrawal from exposure usually results in a normal electroencephalogram within 1 to 6 months. In most cases recovery is rapid, but headache, dizziness, lethargy, weakness, and anorexia may persist

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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for 2 to 4 weeks. In less severe cases of endrin intoxication, the complaints are headache, dizziness, abdominal discomfort, nausea, vomiting, insomnia, agitation and, occasionally, slight mental confusion. There are numerous reports of fatalities from ingestion of endrin. In one nonfatal incident, ingestion of bread made with endrin-contaminated flour resulted in sudden convulsions in three people; in one person the serum endrin level was 0.053 ppm 30 minutes after the convulsion and 0.038 ppm after 20 hours; in the other two cases no endrin was detected in the blood at 8.5 or 19 hours, respectively, after convulsions.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 380.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of endrin): Not applicable
5. Melting point: 200 C (392 F) decomposes
6. Vapor pressure at 20 C (68 F): 0.0000002 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 160 ppb
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 200 C (392 F) cause a chemical change that gives off heat and may cause containers to burst. If a solvent is present, flammable vapors may be formed from it.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause evolution of heat and formation of explosive solvent vapors.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, other volatile chlorinated compounds, and carbon monoxide) may be released when endrin decomposes.
4. Special precautions: None

- **Flammability**

1. Solid not combustible; may be dissolved in flammable solvent

- **Warning properties**

Since the vapor pressure of endrin is negligible, warning properties are not considered.

Endrin is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for endrin is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with endrin or liquids containing endrin.
- If employees' clothing has had any possibility of being contaminated with endrin or liquids containing endrin, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with endrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of endrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the endrin, the person performing the operation should be informed of endrin's hazardous properties.
- Where there is any possibility of exposure of an employee's body to endrin or liquids containing endrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with endrin should be removed immediately and not reworn until the endrin is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is

any possibility of endrin or liquids containing endrin contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to endrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with endrin should be immediately washed or showered with soap or mild detergent and water to remove any endrin.
- Workers subject to skin contact with endrin or liquids containing endrin should wash with soap or mild detergent and water any areas of the body which may have contacted endrin at the end of each work day.
- Eating and smoking should not be permitted in areas where endrin or liquids containing endrin are handled, processed, or stored.
- Employees who handle endrin or liquids containing endrin should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to endrin may occur and control methods which may be effective in each case:

Operation	Controls
Application as an insecticide on cotton fields and vegetable crops, and as a rodenticide against mice and chipmunks in orchards	Personal protective equipment
Formulation for use as an insecticide and rodenticide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of endrin	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If endrin or liquids containing endrin get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If endrin or liquids containing endrin get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If endrin or liquids containing endrin penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of endrin, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When endrin or liquids containing endrin have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If endrin is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing endrin should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Endrin may be disposed of in sealed containers in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on endrin, look up endrin in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR ENDRIN

Condition	**Minimum Respiratory Protection*** **Required Above 0.1 mg/m^3**
Particulate Concentration	
1 mg/m^3 or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m^3** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of endrin; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Epichlorohydrin*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_3H_5OCl
- Synonyms: 1-Chloro-2,3-epoxypropane; 2-chloropropylene oxide; gamma-chloropropylene oxide
- Appearance and odor: Colorless liquid with an irritating chloroform-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for epichlorohydrin is 5 parts of epichlorohydrin per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 19 milligrams of epichlorohydrin per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 2 mg/m^3 (0.5 ppm) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 19 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Epichlorohydrin should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Epichlorohydrin can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Epichlorohydrin may cause irritation of the eyes, respiratory tract, and skin. Nausea and vomiting may also occur. Coughing, difficult breathing, and a blue coloration of the skin may be present. Liquid epichlorohydrin may produce blistering and deep-seated pain on contact with the skin. The liquid is highly irritating to the eyes. Breathing difficulty may occur several hours after exposure. A person may become sensitized to this chemical so that even very small amounts cannot be tolerated.

2. Long-term Exposure: Repeated or prolonged skin contact with epichlorohydrin may cause skin burns. Repeated or prolonged contact with this chemical might also cause liver, lung, and kidney injury. Antifertility effects, including persistent sterility, have been induced in animals exposed to epichlorohydrin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to epichlorohydrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to epichlorohydrin at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, hematopoetic and respiratory systems, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Epichlorohydrin may cause human lung damage. Surveillance of the lungs is indicated.

—Pulmonary function testing of FVC and FEV (1 sec): Epichlorohydrin is a severe pulmonary irritant in animals.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Eye disease: Epichlorohydrin is a severe eye irritant and may cause tissue damage. Those with pre-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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existing eye problems may be at increased risk from exposure.

—Liver function tests: Epichlorohydrin may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Epichlorohydrin is a defatting agent and can cause dermatitis on prolonged exposure. It can also cause burning, itching, blisters, skin erosion, redness, and residual erythema which may occur from a few minutes to several hours after exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Medical warning: Employees should be informed that large doses of epichlorohydrin have caused antifertility effects in animals; however, no effects have been found on potency.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Epichlorohydrin vapor is a potent eye and respiratory irritant. The LC50 for rats was 500 ppm for 4 hours; the animals showed gradual development of cyanosis followed by muscular relaxation of the extremities, but not narcosis. Rats exposed repeatedly to 120 ppm for 6-hour periods showed lung, liver, and kidney injury; some respiratory distress was observed at 56 ppm, while 9 ppm produced no effects. The liquid is markedly irritating when instilled in the eye and intensely irritating to the depilated skin of laboratory animals, leading to widespread necrosis. Subcutaneous injection of epichlorohydrin in animals has been reported to cause sarcoma at the site of injection. In man, contact of the liquid with the skin at first produces a slight transient burning sensation which may be followed several hours later by blistering and pain in the region of contact; it is also highly irritating to the eyes. An occasional case of sensitization with resulting intolerance to very small quantities of the substance has been reported. At 25 ppm the odor is recognized by the majority of persons; one report indicated eye and nose irritation only at levels exceeding 100 ppm while another stated that 40 ppm at the site of a spill caused immediate eye, nose, and throat irritation. The earliest symptoms of intoxication may be referable to the gastrointestinal tract (nausea, vomiting, abdominal discomfort) or pain in the region of the liver; labored breathing, cough, and cyanosis may be evident; the onset of chemical pneumonitis may occur several hours after exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 92.5
2. Boiling point (760 mm Hg): 115 C (239 F)
3. Specific gravity (water = 1): 1.18
4. Vapor density (air = 1 at boiling point of epichlorohydrin): 3.19
5. Melting point: −58 C (−72 F)
6. Vapor pressure at 20 C (68 F): 13 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 6.4
8. Evaporation rate (butyl acetate = 1): 1.35

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 325 C (617 F) will cause epichlorohydrin to polymerize.
2. Incompatibilities: Contact with strong acids, caustics, zinc, aluminum, chlorides of iron and aluminum and strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving epichlorohydrin.
4. Special precautions: Epichlorohydrin will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 37.8 C (100 F) (closed cup)
2. Autoignition temperature: 415.6 C (780 F)
3. Flammable limits in air, % by volume: Lower: 3.8; Upper: 21.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

The AIHA *Hygienic Guide* states that 5 ppm of epichlorohydrin, the permissible exposure limit, cannot be detected by odor. At 16 ppm, four humans "detected the presence of epichlorohydrin, but only two could identify it;" at 64 ppm, all four could recognize the odor. In another investigation, half of a group of people detected 10-12 ppm, and within 5 minutes all of the subjects detected 25 ppm. According to the *Hygienic Guide*, "the threshold for nose and eye irritation is reported to be greater than 100 ppm." Since the warning properties of epichlorohydrin do not become evident until concentrations are several times the permissible exposure limit, epichlorohydrin is treated as a material with poor warning properties.

Epichlorohydrin is an eye irritant. The NIOSH Criteria Document cites data indicating that exposure to 20 ppm for one hour causes temporary burning of the eye and nasal passages.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- ***Ceiling Evaluation***

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of epichlorohydrin. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure epichlorohydrin may be used. An analytical method for epichlorohydrin is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid epichlorohydrin.
- Clothing contaminated with liquid epichlorohydrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of epichlorohydrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the epichlorohydrin, the person performing the operation should be informed of epichlorohydrin's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid epichlorohydrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid epichlorohydrin should be removed immediately and not reworn until the epichlorohydrin is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid epichlorohydrin contacting the eyes.
- Where there is any possibility that employee's eyes may be exposed to liquid epichlorohydrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid epichlorohydrin should be immediately washed or showered with soap or mild detergent and water to remove any epichlorohydrin.
- Eating and smoking should not be permitted in areas where liquid epichlorohydrin is handled, processed, or stored.
- Employees who handle liquid epichlorohydrin should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to epichlorohydrin may occur and control methods which may be effective in each case:

Operation	**Controls**
Use as intermediate in manufacture of DGEBA resins, epoxy novolac resins, phenoxy resins, and wet-strength resins for paper	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of glycerol and glycidol derivatives for use as as plasticizer, stabilizer solvent, intermediate, dyestuff surfactants, pharmaceuticals, and intermediates for further synthesis	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use as stabilizer in manufacture of chlorinated rubber and chlorinated insecticides	Process enclosure; local exhaust ventilation; personal protective equipment
Use in coating fibers and textile surface coatings	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If epichlorohydrin gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If epichlorohydrin gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water. If epichlorohydrin soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of epichlorohydrin, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When epichlorohydrin has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If epichlorohydrin is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Epichlorohydrin should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of epichlorohydrin vapors are permitted.

- Waste disposal method:

Epichlorohydrin may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 11, 1976, and Volume 18, 1978.

RESPIRATORY PROTECTION FOR EPICHLOROHYDRIN

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
*Greater than 250 ppm**** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and acid gases. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of epichlorohydrin; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 250 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for EPN

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(4\text{-}NO_2C_6H_4O)(C_2H_5O)C_6H_5PSo$ $C_{14}H_{14}NO_4PS$
- Synonyms: O-ethyl O-p-nitrophenyl thionobenzenephosphonate; O-ethyl O-p-nitrophenyl benzenephosphonothioate
- Appearance: Yellow solid or brown liquid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for EPN is 0.5 milligram of EPN per cubic meter of air (mg/m³) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

EPN can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of EPN, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing EPN, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur, usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to all the above symptoms, weakness, generalized twitching, and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, slow heartbeat, convulsions and coma may occur.

2. Long-term Exposure: Repeated exposure to EPN may make a person more susceptible to the effects of this and related chemicals. Repeated exposure to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to EPN.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to EPN at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Cholinesterase determination: EPN causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to any new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed quarterly or at any

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time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

EPN is an anticholinesterase agent; absorption may occur from inhalation of the dust or mist, from skin absorption of solutions, or from ingestion. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscle, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms may occur promptly or may be delayed for up to 12 hours. After inhalation, respiratory and ocular effects are the first to appear, , often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects, such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur, usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for weeks after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects. In animals, EPN has produced a demyelination syndrome.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 323.3
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity (water = 1): 1.27
  4. Vapor density (air = 1 at boiling point of EPN): Not applicable
  5. Melting point: 36 C (97 F)
  6. Vapor pressure at 20 C (68 F): 0.0003 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None.
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of sulfur and nitrogen, phosphoric acid mist, and carbon monoxide) may be released when EPN decomposes.
  4. Special precautions: Liquid EPN will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of EPN.
  2. Eye Irritation Level: EPN is not known to be an eye irritant.
  3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of EPN, it is treated as a material with poor warning properties. The Pennsylvania *Hygienic Information Guide* for EPN states that the "lack of odor and warning signs, as well as the delayed onset of symptoms, make EPN a dangerous material to work with."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of EPN using a filter with subsequent recovery with iso-octane and gas chromatrographic analysis. A detailed analytical method for EPN may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set T" (order number PB 262 404).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with EPN or liquids containing EPN.
- If employees' clothing has had any possibility of being contaminated with EPN or liquids containing EPN, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with EPN should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of EPN from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the EPN, the person performing the operation should be informed of EPN's hazardous properties.
- Where there is any possibility of exposure of an employee's body to EPN or liquids containing EPN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with EPN should be removed immediately and not reworn until the EPN is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of EPN or liquids containing EPN contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to EPN or liquids containing EPN, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with EPN should be immediately washed or showered with soap or mild detergent and water to remove any EPN.
- Workers subject to skin contact with EPN or liquids containing EPN should wash with soap or mild detergent and water any areas of the body which may have contacted EPN at the end of each work day.
- Eating and smoking should not be permitted in areas where EPN or liquids containing EPN are handled, processed, or stored.
- Employees who handle EPN or liquids containing EPN should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to EPN may occur and control methods which may be effective in each case:

Operation	Controls
Formulation for use as an insecticide and acaricide	Process enclosure; dust collection; personal protective equipment; general dilution ventilation
Application as an insecticide and acaricide on agricultural crops, vegetables, fruit trees, and ornamentals	Material substitution; personal protective equipment
Manufacture of EPN	Process enclosure; general dilution ventilation; personal protective equipment; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If EPN or liquids or mists containing EPN get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If EPN or liquids or mists containing EPN get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If EPN or liquids or mists containing EPN penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of EPN, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When EPN or liquids containing EPN have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If EPN is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Cover with soda ash, mix and spray with water. Place in a container of water and allow to stand for two days, then neutralize with 6 molar HCl.

- Waste disposal method:

EPN may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR EPN

Condition	**Minimum Respiratory Protection*** **Required Above 0.5 mg/m³**
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of EPN; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 50 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethanolamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HOCH_2CH_2NH_2$
- Synonyms: Ethylolamine; monoethanolamine; beta-aminoethyl alcohol; 2-aminoethanol; 2-hydroxyethylamine
- Appearance and odor: Colorless liquid with a mild ammonia-like odor. It can be a solid below 10.3 C (51 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethanolamine is 3 parts of ethanolamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of ethanolamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethanolamine can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Ethanolamine may cause nose, eye, and skin irritation.

2. Long-term Exposure: Prolonged or repeated skin contact with liquid ethanolamine may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethanolamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethanolamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethanolamine exposure.

—Skin disease: Ethanolamine may cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Ethanolamine causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Ethanolamine causes kidney damage in animals and this justifies special consideration before exposing those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethanolamine might cause exacerbation of symptoms.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethanolamine vapor is a skin, eye, and respiratory irritant, and has significant narcotic properties. In animals exposed repeatedly to 66 to 100 ppm, some animals died during 24 to 30 days of exposure, and all animals were lethargic. Dogs and cats exposed to 2.47 mg/l (990 ppm) for 4 days survived but four of six guinea pigs died from exposure to 0.58 mg/l (233 ppm) for 1 hour; pathologic changes were chiefly those of pulmonary irritation, with some non-specific changes in the liver and kidneys. No mortality or pathology resulted from 90 days of continuous exposure of dogs to 26 ppm, of rats to 12 ppm, or of guinea pigs to 15 ppm. The liquid produced moderate irritation of the skin of rabbits and

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severe irritation in the eyes of rabbits. When applied to human skin for 1-½ hours, marked redness of the skin occurred. No systemic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 61.1
2. Boiling point (760 mm Hg): 170 C (338 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of ethanolamine): 2.1
5. Melting point: 10.3 C (51 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving ethanolamine.
4. Special precautions: Liquid ethanolamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 85 C (185 F) (closed cup)
2. Autoignition temperature: 780 C (1436 F)
3. Flammable limits in air, % by volume: Lower: 5.5 (calculated); Upper: 17 (estimated)
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Ethanolamine has a mild ammonia-like odor, which the AIHA *Hygienic Guide* reports is noticeable at 2 to 3 ppm.
2. Eye Irritation Level: The *Hygienic Guide* states that ethanolamine is an eye irritant, but do not specify whether both liquid and vapor have this effect. Grant reports that "a drop of ethanolamine applied to rabbit eyes causes injury similar to that caused by ammonia, but slightly less severe." The available literature does not specifically report that the vapor of ethanolamine produces eye irritation. By analogy with ammonia, ethanolamine is treated as an eye irritant for the purposes of this guideline.
3. Other Information: The *Hygienic Guide* reports that ethanolamine is a respiratory tract irritant. The concentrations producing this irritation are not given.
4. Evaluation of Warning Properties: Since ethanolamine has an odor threshold which is at or below the permissible exposure limit, it is treated as a substance with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for ethanolamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid or solid ethanolamine.
- If employees' clothing may have become contaminated with solid ethanolamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with liquid or solid ethanolamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethanolamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethanolamine, the person performing the operation should be informed of ethanolamine's hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid or solid ethanolamine should be removed promptly and not reworn until the ethanolamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid or solid ethanolamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid or solid ethanolamine, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid or solid ethanolamine should be promptly washed or showered to remove any ethanolamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethanolamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of monoalkanolamides for nonionic detergents, emulsifiers, and soaps; fuel oil additives; water-in-oil emulsifiers; pharmaceuticals; agricultural chemicals; cosmetics; emulsion paints; polishers, and cleansers	Process enclosure; local exhaust ventilation
Use during synthesis of acelethanolamine in manufacture of inks, paper, glues, textiles, and polishes; syntheses of phenylethanolamine for acetate rayon dyes, dyestuffs; synthesis of tolyethanolamine in emulsifiers and dyestuffs	Process enclosure; local exhaust ventilation
Use during synthesis of 2-mercaptothiazole in rubber vulcanization acceleration	Process enclosure; local exhaust ventilation; personal protective equipment
Use in recovery and removal of acid gases from natural, fuel, and process gas in synthesis of ammonia; use in dry ice manufacture	Process enclsoure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethanolamine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethanolamine gets on the skin, promptly flush the contaminated skin with water. If ethanolamine soaks through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethanolamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethanolamine has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethanolamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. If in liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

4. If in solid form, allow to melt and follow (3) above.

- Waste disposal methods:

Ethanolamine may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHANOLAMINE

Condition	**Minimum Respiratory Protection* Required Above 3 ppm**
Vapor Concentration	
30 ppm or less	A chemical cartridge respirator which provides protection against ethanolamine.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
150 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) which provides protection against ethanolamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against ethanolamine.
1000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against ethanolamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHION

INTRODUCTION

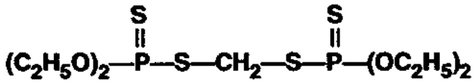
This guideline summarizes pertinent information about ethion for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{22}O_4P_2S_4$

- **Structure**



$(C_2H_5O)_2-\overset{\overset{S}{\|}}{P}-S-CH_2-S-\overset{\overset{S}{\|}}{P}-(OC_2H_5)_2$

- **Synonyms**

bis(S-(Diethoxyphosphinothioyl)mercapto)methane; ethyl methylene phosphorodithioate; O,O,O',O'-tetraethyl S,S'-methylene di(phosphorodithioate); phosphorodithioic acid, O,O-diethyl ester, S,S-diester with methanedithiol; Bladan; Diethion; Embathion; Ethanox; Ethodan; Fosfono 50; Hylemox; Niagra 1240; Nialate; Rhodiacide; Rhodocide; Soprathion

- **Identifiers**

1. CAS No.: 563-12-2
2. RTECS No.: TE4550000
3. DOT NA: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Ethion is a colorless liquid that is odorless when pure. Ethion is marketed in several forms: as granules, a wettable powder, a dust, and in various oil solutions and combinations with other materials. Technical grade ethion has a very disagreeable odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 384.48
2. Boiling point (760 mm Hg): Decomposes above 150°C (302°F)
3. Specific gravity (water = 1): 1.22 at 20°C (68°F)
4. Vapor density: Data not available
5. Freezing/melting point: -12° to -13°C (8.6° to 10.4°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 25°C (77°F): 0.0000015 mm Hg

7. Solubility: Slightly soluble in water; soluble in acetone, methyl alcohol, ethyl alcohol, xylene, chloroform, methylated naphthalene, and petroleum oils.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Ethion is incompatible with alkaline formulations.

3. Hazardous decomposition products: Toxic gases (such as oxides of sulfur and phosphorus) may be released in a fire involving ethion.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a fire hazard rating for ethion.

1. Flash point: 176°C (348.8°F)

2. Autoignition temperature: Data not available

3. Flammable limits: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving ethion. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving ethion should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of ethion may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethion. Chemical protective clothing that is specifically recommended for ethion may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving ethion.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethion [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.4 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for ethion. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ethion a threshold limit value (TLV) of 0.4 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to ethion [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cholinesterase inhibition and toxic effects on the nervous, respiratory, and digestive systems associated with ethion exposure [NIOSH 1992]. The ACGIH limit is based on the risk of organophosphate poisoning associated with exposure to ethion [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ethion can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Ethion is an organophosphate pesticide that produces its effects by inhibiting cholinesterase activity in the central nervous system.

Instilled into the eyes of rabbits, 0.05 ml of ethion caused immediate irritation without corneal injury [NLM 1993]. The dermal LD_{50} is 62 mg/kg in rats and 915 mg/kg in guinea pigs [NIOSH 1993]. The LC_{50} in rats is 864 mg/m3 for an unspecified period [NIOSH 1993]. The oral LD_{50} is 13 mg/kg in rats and 40 mg/kg in mice [NIOSH 1993]. Rats fed ethion at a dietary level of 300 ppm for 28 days developed marked cholinesterase inhibition, and those fed dietary levels of 600 to 1,500 ppm showed complete cholinesterase inhibition [NLM 1993].

2. *Effects on Humans:* Ethion is an organophosphate pesticide that causes cholinesterase inhibition in humans. The lethal oral dose in humans is estimated to be 50 to 500 mg/kg [Gosselin et al. 1984]. Ethion is reported to have caused organophosphate poisoning in peach and grape pickers who were applying this pesticide [ACGIH 1991]. In an in vitro culture, ethion caused a significant increase in the frequency of sister chromatid exchanges in human lymphoid cells [NLM 1993].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute oral exposure causes severe gastrointestinal effects, such as cramps, diarrhea, nausea, and anorexia. Acute inhalation causes wheezing, difficult breathing, blurred vision, constricted pupils, and tearing. Acute dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Repeated exposure to small amounts of ethion may cause acetylcholine buildup and lead to the signs and symptoms of poisoning described above for acute exposure.

- **Emergency procedures:**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately*** rinse concentrated solutions, vapors, mists, or aerosols of ethion from the eyes with large amounts of water for at least 15 min, occasionally lifting the lower and upper eyelids. If irritation persists, get medical attention as soon as possible.

2. *Skin exposure:* Ethion can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion esposure:* Take the following steps if ethion or a solution containing this substance is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ethion and lead to worker exposures to this substance:

—Use as an insecticide and acaricide for citrus fruit, apples, nuts, deciduous fruit, and cotton

—Use as a cattle dip for ticks and as a treatment for buffalo flies

—Use for the control of aphids, mites, scales, thrips, leafhoppers, maggots, and foliar feeding larvae on a wide variety of food, fiber, and ornamental crops

The following methods are effective in controlling worker exposures to ethion, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to ethion, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on red blood cell and plasma cholinesterase activity.

  A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ethion at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reductions in red blood cell or plasma cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ethion exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethion on red blood cell or plasma cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific qualitative indicator of exposure to organophosphorus chemicals such as ethion. Inhibition of RBC ChE can be an indicator either of acute overexposure or of cumulative chronic exposure, depending on the intensity and duration of exposure. Individual pre-exposure levels of enzyme activities should be determined by measuring RBC ChE activity in blood samples collected on two occasions (at least 3 days apart) before exposure begins or following at least 30 days without exposure; the same method and laboratory should be used for sampling and analysis. An RBC ChE activity level that is equal to 70 percent of the individual's baseline is recommended by some sources as a Biological Exposure Index (BEI) for exposure to organophosphorus chemicals.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne ethion is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 480 liters is collected. The sample is then treated with toluene to extract the ethion. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in the OSHA Computerized Information System [OSHA 1993] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

Ethion can be absorbed through the skin in toxic amounts. Therefore, if ethion contacts the skin, workers should wash the affected areas repeatedly and vigorously with soap and water.

Clothing contaminated with ethion should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of ethion, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles ethion should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where ethion or a solution containing ethion is handled, processed, or stored.

STORAGE

Ethion should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of ethion should be protected from physical damage and should be stored separately from food or feed products, heat, sparks, and open flame. Because containers that formerly contained ethion may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethion, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the ethion for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous waste, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  The owners or operators of a facility must comply with EPA's emergency planning requirements [40 CFR 355.30] if 1,000 lb or more of ethion are present.

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for ethion is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of ethion emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although ethion is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ethion exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only those respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with ethion. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon has been tested for use against permeation by ethion and may provide protection for periods greater than 4 but less than 8 hours. Natural rubber has a breakthrough time of less than 1 hr and is therefor not recommended for use against permeation by ethion.

If ethion is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ethion might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ethion.

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Gosselin RE, Smith RP, Hodge HC [1984]. Clinical toxicology of commercial products. 5th ed. Baltimore, MD: Williams & Wilkins.

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NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

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Occupational Health Guideline for 2-Ethoxyethanol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5OCH_2CH_2OH$
- Synonyms: Ethyleneglycol monoethyl ether; Cellosolve (R) solvent
- Appearance and odor: Colorless liquid with a sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2-ethoxyethanol is 200 parts of 2-ethoxyethanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 740 milligrams of 2-ethoxyethanol per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for 2-ethoxyethanol from 100 ppm to 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Ethoxyethanol can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

In animal experiments 2-ethoxyethanol has caused liver, kidney, and lung damage and anemia due to the destruction of red blood cells. It has also caused irritation of the eyes.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2-ethoxyethanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2-ethoxyethanol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 2-ethoxyethanol exposure.

—Chronic respiratory disease: 2-Ethoxyethanol causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 2-ethoxyethanol might cause exacerbation of symptoms due to its irritant properties.

—Blood disease: 2-Ethoxyethanol causes in animals an increase in red cell fragility, decreased levels of red cells and hemoglobin, and an increase in immature white cells. Persons with anemia may be at increased risk from exposure.

—Kidney disease: 2-Ethoxyethanol causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: 2-Ethoxyethanol is absorbed through the skin. Persons with chronic skin disorders characterized by eczema or fissures may be at added risk of absorption of toxic amounts.

—Liver disease: Although 2-ethoxyethanol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Summary of toxicology**

2-Ethoxyethanol vapor is toxic to the lungs, kidneys, and hematopoietic system in animals. In mice the LC50 for 7 hours was 1820 ppm; death was attributed to lung and kidney injury. In rabbits, repeated daily doses of 1 ml/kg given orally caused albuminuria and hematuria on the 7th day with death on the 8th day due to kidney injury. Dogs repeatedly exposed to 840 ppm for 12 weeks developed a slight decrease in red cells and hemoglobin and an increase in immature white cells. In female rats exposed to 125 ppm for 4 hours, there was an increase in erythrocyte fragility. Of two workers employed for 3 years in factories using 2-ethoxyethanol as a solvent, one had a slight yellowish discoloration of the sclera and the other had trace albuminuria and a slightly increased level of bilirubin in the blood. The liquid instilled in the eyes of animals caused immediate discomfort, some conjunctival irritation, and a slight transitory irritation of the cornea which was readily reversible. Repeated and prolonged contact of the liquid with the skin of rabbits caused only a mild irritation, but toxic amounts were readily absorbed through the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 90.1
2. Boiling point (760 mm Hg): 135 C (275 F)
3. Specific gravity (water = 1): 0.93
4. Vapor density (air = 1 at boiling point of 2-ethoxyethanol): 3.0
5. Melting point: −70 C (−94 F) (pour point)
6. Vapor pressure at 20 C (68 F): 4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving 2-ethoxyethanol.
4. Special precautions: 2-Ethoxyethanol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 49 C (120 F) (closed cup)
2. Autoignition temperature: 235 C (455 F)
3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 14
4. Extinguishant: "Alcohol" foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that 2-ethoxyethanol has "a slight odor at low concentrations and a disagreeable odor at high concentrations." Grant states that this substance "is a practically odorless liquid."
2. Eye Irritation Level: Grant states that "exposure of rabbits to high vapor concentrations causes symptoms of ocular and respiratory irritation, but even at concentrations which are probably lethal, causes no significant ocular injury."
3. Other Information: The *Hygienic Guide* states that "high vapor concentrations can cause irritation of the nose and throat." No quantitative information is available, however, concerning the thresholds of irritation.
4. Evaluation of Warning Properties: Since eye, nose and throat irritation occur only at high levels, and since Grant points out that this substance is almost odorless, 2-ethoxyethanol is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on *a single eight-hour sample* or *on two four-hour* samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 2-ethoxyethanol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 2-ethoxyethanol.

- Clothing wet with 2-ethoxyethanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-ethoxyethanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2-ethoxyethanol, the person performing the operation should be informed of 2-ethoxyethanol's hazardous properties.
- Non-impervious clothing which becomes contaminated with 2-ethoxyethanol should be removed promptly and not reworn until the 2-ethoxyethanol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 2-ethoxyethanol may contact the eyes.

SANITATION

- Skin that becomes contaminated with 2-ethoxyethanol should be promptly washed or showered to remove any 2-ethoxyethanol.
- Employees who handle liquid 2-ethoxyethanol should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2-ethoxyethanol may occur and control methods which may be effective in each case:

Operation	Controls
Use as solvent in manufacture of lacquers, lacquer thinners, nitrocellulose lacquers, alkyd resins, printing ink solvents, varnish removers, cleaning compounds, soaps, cosmetics, pesticides, pharmaceuticals, adhesives, and detergents; during use in textile dyeing and printing and manufacture of leather finishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as anti-icing additive in manufacture of brake fluids, aviation fuels, and automotive anti-stall additives	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid 2-ethoxyethanol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid 2-ethoxyethanol gets on the skin, promptly flush the contaminated skin with water. If liquid 2-ethoxyethanol soaks through the clothing, promptly flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 2-ethoxyethanol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 2-ethoxyethanol has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 2-ethoxyethanol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. 2-Ethoxyethanol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers

designed to preclude the formation of explosive concentrations of 2-ethoxyethanol vapors are permitted.

- Waste disposal methods:

2-Ethoxyethanol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "2-Ethoxyethanol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Ethylene Glycol Monomethyl Ether," *Hygienic Guide Series*, Detroit, Michigan, 1957.
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- Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.

RESPIRATORY PROTECTION FOR 2-ETHOXYETHANOL

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
6000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or continuous-flow mode.
Greater than 6000 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of 2-ethoxyethanol; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 6000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for 2-Ethoxyethylacetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5OCH_2CH_2OCOCH_3$
- Synonyms: Cellosolve acetate; glycol monoethyl ether acetate; ethylene glycol monoethyl ether acetate
- Appearance and odor: Colorless liquid with a mild, non-residual odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2-ethoxyethylacetate is 100 parts of 2-ethoxyethylacetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 540 milligrams of 2-ethoxyethylacetate per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for 2-ethoxyethylacetate from 100 ppm to 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Ethoxyethylacetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

High air concentrations of 2-ethoxyethylacetate may cause irritation of the eyes and nose. The material is not very toxic when swallowed, but if a large enough dose is swallowed, death may result. It is not very toxic when inhaled in amounts likely to be encountered under ordinary conditions, but inhaling large amounts might cause vomiting, kidney damage, paralysis, and death. The material may be absorbed through the skin and, if a large amount of it is absorbed in this way, death may result.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2-ethoxyethylacetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2-ethoxyethylacetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 2-ethoxyethylacetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 2-ethoxyethylacetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: 2-Ethoxyethylacetate is absorbed through the skin. It also is a defatting agent and may cause dryness and cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although 2-ethoxyethylacetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Liver disease: Although 2-ethoxyethylacetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

High concentrations of 2-ethoxyethylacetate vapor are

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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irritating to the eyes and mucous membranes. Guinea pigs and rabbits survived exposure to saturated vapor-air mixtures (4000 ppm) for 1 hour, but two such exposures for 4 to 6 hours caused delayed death to cats.

There was narcosis before death in these animals, and damage to the kidneys was found at autopsy. This agent is absorbed through the skin. Lethal doses have been administered through the skin to rabbits. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 132
2. Boiling point (760 mm Hg): 156 C (313 F)
3. Specific gravity (water = 1): 0.98
4. Vapor density (air = 1 at boiling point of 2-ethoxyethylacetate): 4.6
5. Melting point: −62 C (−80 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 23
8. Evaporation rate (butyl acetate = 1): 0.2

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving 2-ethoxyethylacetate.
4. Special precautions: None

- **Flammability**

1. Flash point: 47 C (117 F) (closed cup)
2. Autoignition temperature: 380 C (716 F)
3. Flammable limits in air, % by volume: Lower: 1.7
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: According to the *Handbook of Organic Industrial Solvents*, the odor of 2-ethoxyethylacetate is detectable at the threshold limit.
2. Eye Irritation Level: According to the *Documentation of TLV's*, dogs exposed to "120 seven-hour inhalations of 600 ppm" experienced eye and nose irritation. No quantitative information is available, however, concerning the threshold of eye irritation. Patty reports that "high concentrations of vapor . . . are irritating to the eyes and nose."
3. Evaluation of Warning Properties: Since the odor of 2-ethoxyethylacetate can be detected at the TLV, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of 2-ethoxyethylacetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 2-ethoxyethylacetate may be used. An analytical method for 2-ethoxyethylacetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 2-ethoxyethylacetate.
- Clothing wet with liquid 2-ethoxyethylacetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-ethoxyethylacetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2-ethoxyethylacetate, the person performing the operation should be informed of 2-ethoxyethylacetate's hazardous properties.

- Non-impervious clothing which becomes wet with 2-ethoxyethylacetate should be removed promptly and not reworn until the 2-ethoxyethylacetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 2-ethoxyethylacetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 2-ethoxyethylacetate should be promptly washed or showered to remove any 2-ethoxyethylacetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2-ethoxyethylacetate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent vehicle during hot and cold spray applications of lacquers and wood stains, including automobiles, airplanes, and metal and wood finishing	Local exhaust ventilation; personal protective equipment
Use in manufacture of varnishes, thinners, lacquers, wood stains, adhesives, varnish removers, fabric coatings, paper coatings, and textile sizing	General dilution ventilation; personal protective equipment
Liberation during manufacture of cellulose acetate films, including transparent wrapping material, safety film, packaging film, and photographic film	General dilution ventilation
Liberation during coating process of fabrics, leather, and paper for waterproofing, sizing, and laminating	General dilution ventilation
Use during dipping application of lacquers and enamels of small articles having rounded or cylindrical shapes, wire flash bulbs, etc.	General dilution ventilation; personal protective equipment
Use during brushing or other hand applications of lacquers, adhesives, enamels, household cement, specialized lacquers, etc.	General dilution ventilation; personal protective equipment
Use during solvent recovery during equipment maintenance, pouring solvent, and refilling containers	General dilution ventilation; personal protective equipment
Use as a solvent for many oils and gums	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 2-ethoxyethylacetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 2-ethoxyethylacetate gets on the skin, promptly flush the contaminated skin with water. If 2-ethoxyethylacetate soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of 2-ethoxyethylacetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 2-ethoxyethylacetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 2-ethoxyethylacetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. 2-Ethoxyethylacetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

2-Ethoxyethylacetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "2-Ethoxyethylacetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR 2-ETHOXYETHYLACETATE (CELLOSOLVE ACETATE)

Condition	**Minimum Respiratory Protection*** ***Required Above 100 ppm***
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOC_2H_5$
- Synonyms: Acetic ester; acetic ether; ethyl ethanoate
- Appearance and odor: Colorless liquid with a pleasant, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl acetate is 400 parts of ethyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1400 milligrams of ethyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl acetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Ethyl acetate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although ethyl acetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl acetate vapor is irritating to the eyes and respiratory passages of man at concentrations above 400 ppm. In animals it has a narcotic effect at concentrations of over 5000 ppm. Due to its irritating properties, employees will not voluntarily remain in such high concentrations. Repeated exposures of rabbits to 4450 ppm for 1 hour daily for 40 days resulted in anemia with leukocytosis, and damage to liver and kidneys. Animals exposed to lethal concentrations died with pulmonary edema

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and hemorrhage. This substance is a defatting agent, and prolonged exposure may cause irritation of the skin. Painful conjunctival irritation may occur from splashes in the eye. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 88
2. Boiling point (760 mm Hg): 77 C (171 F)
3. Specific gravity (water = 1): 0.9
4. Vapor density (air = 1 at boiling point of ethyl acetate): 3.0
5. Melting point: −83 C (−117 F)
6. Vapor pressure at 20 C (68 F): 76 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.7
8. Evaporation rate (butyl acetate = 1): 6

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, or strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl acetate.
4. Special precautions: Ethyl acetate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −4.4 C (24 F) (closed cup)
2. Autoignition temperature: 427 C (800 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 11
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: May and Summer report odor thresholds for ethyl acetate of 0.0056 ppm and 50 ppm, respectively.
2. Eye Irritation Level: Grant states that "a concentration of 400 ppm in air causes a sensation of irritation in human eyes." Animals exposed to much higher concentrations developed no corneal damage, only conjunctival irritation.
3. Evaluation of Warning Properties: Through its odor and irritant effects, ethyl acetate can be detected below or at the permissible exposure limit. For the purposes of this guideline, ethyl acetate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl acetate may be used. An analytical method for ethyl acetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl acetate.
- Clothing wet with liquid ethyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl acetate, the person performing the operation should be informed of ethyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid ethyl acetate should be removed immediately and not reworn until the ethyl acetate is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid ethyl acetate should be promptly washed or showered to remove any ethyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use of shellacs, lacquers, dopes, varnishes, and stains	Local exhaust ventilation; general dilution ventilation
Liberation during manufacture of smokeless powder; during manufacture of artificial leather; during preparation of photographic films	Process enclosure; general dilution ventilation
Liberation and use as a solvent during application of coatings containing nitrocellulose, cellulose acetate, shellac, synthetic rubber, vinyl resins, and inks	Process enclosure; general dilution ventilation
Use as a cleaning agent in textile industry	Process enclosure; general dilution ventilation
Liberation during manufacture of photographic film	Process enclosure; general dilution ventilation
Liberation during manufacture of linoleum and plastic wood; during manufacture of dyes, drug intermediates, ethyl acetoacetate, etc.; during use of duplicator fluid	Process enclosure; general dilution ventilation
Liberation during use of varnish removers	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl acetate gets on the skin, promptly flush the contaminated skin with water. If ethyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Ethyl acetate should not be allowed

to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Ethyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethyl Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR ETHYL ACETATE

Condition	**Minimum Respiratory Protection*** **Required Above 400 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in *pressure-demand or other positive pressure mode.*
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Acrylate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_2=CHCOOC_2H_5$
- Synonyms: Ethyl propenoate
- Appearance and odor: Colorless liquid with a sharp, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl acrylate is 25 parts of ethyl acrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of ethyl acrylate per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for ethyl acrylate from 25 ppm to 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl acrylate can affect the body if it is inhaled, comes in contact with the eyes or skin., or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl acrylate may cause irritation of the eyes, nose, throat, and lungs. Death may be caused by lung damage from breathing high air levels or from swallowing it.

2. Long-term Exposure: Prolonged contact with the skin or eyes may result in severe damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl acrylate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl acrylate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl acrylate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl acrylate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Ethyl acrylate is absorbed through the skin. It also is a defatting agent and may cause dryness or cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethyl acrylate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although ethyl acrylate is not known as a kidney toxin in humans, the importance of this organ in the excretion of certain chemicals and their metabolites should be considered before exposing persons with impaired kidney function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapor of ethyl acrylate is irritating to the conjunctiva and upper respiratory tract. In moderate concentrations there are characteristic lacrimatory effects in man. Animals exposed to high concentrations show marked

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irritation of the eyes and of the respiratory tract, leading to pulmonary edema. The lowest concentration of vapor producing no significant effect in rodents is 75 ppm. A concentration of 2000 ppm vapor killed rats in 4 hours, with death attributable to severe pulmonary irritation, although 1000 ppm for 4 hours allowed survival. Prolonged contact with the skin in animals causes moderate damage, and skin sensitization may occur. Fatal doses are absorbed through the skin of animals exposed for 24 hours. While there are no reports of injury to man from long-term exposure to concentrations ordinarily encountered in the work situation, common practice suggests that most workmen do not tolerate exposure to 25 ppm for more than a few minutes.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): 99 C (211 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of ethyl acrylate): 3.45
5. Melting point: −75 C (−103 F)
6. Vapor pressure at 20 C (68 F): 29.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): 3.3

- **Reactivity**

1. Conditions contributing to instability: Heat and/or lack of appropriate inhibitor concentration can cause ethyl acrylate to polymerize violently and burst container.
2. Incompatibilities: Contact with oxidizing materials, including peroxides and other initiators of polymerization, strong alkalies, and atmospheric moisture may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl acrylate.
4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.

- **Flammability**

1. Flash point: 9 C (48 F) (closed cup)
2. Autoignition temperature: 383 C (721 F)
3. Flammable limits in air, % by volume: Lower: 1.8
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of ethyl acrylate vapor is readily detectable at 1 ppm and was described as fairly strong and moderately irritating at 4 ppm." The Manufacturing Chemists Association reports that an odor of ethyl acrylate can be detected by most persons at 8 ppm.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "a concentration of 272 ppm ethyl acrylate vapor caused irritation of the conjunctiva of rabbit eyes, but 75 ppm did not elicit any observable reaction." According to the MCA, however, irritation of the eyes occurs at about 75 ppm.
3. Other Information: The MCA states that irritation of the mucous membranes occurs at 75 ppm. The AIHA *Hygienic Guide* states that the TLV (25 ppm) "is considered to be too high to prevent irritating effects in humans."
4. Evaluation of Warning Properties: Through its odor ethyl acrylate can be detected below the permissible exposure limit, and through its irritant effects it can be detected at or just several times above the TLV. Therefore, the substance is considered to have good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl acrylate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl acrylate may be used. An analytical method for ethyl acrylate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl acrylate.
- Clothing wet with liquid ethyl acrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl acrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl acrylate, the person performing the operation should be informed of ethyl acrylate's hazardous properties.
- Where exposure of an employee's body to liquid ethyl acrylate may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with liquid ethyl acrylate or non-impervious clothing which becomes contaminated with liquid ethyl acrylate should be removed immediately and not reworn until the ethyl acrylate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl acrylate may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid ethyl acrylate should be promptly washed or showered with soap or mild detergent and water to remove any ethyl acrylate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl acrylate may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of acrylic resins for use in paint formulations, industrial coatings, and latexes; use in manufacture of plastics such as ethylene ethyl acrylate	Local exhaust ventilation; personal protective equipment
Use in manufacture of polyacrylate elastomers and acrylic rubber	Local exhaust ventilation; personal protective equipment
Use in forming of denture materials	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl acrylate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl acrylate gets on the skin, immediately flush the contaminated skin with water. If ethyl acrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl acrylate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl acrylate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl acrylate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Ethyl acrylate should not be allowed

to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Ethyl acrylate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethyl Acrylate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies - Ethyl Acrylate*, New York, 1971.

RESPIRATORY PROTECTION FOR ETHYL ACRYLATE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ethyl acrylate; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5NH_2$
- *Synonyms:* Ethylamine, anhydrous; aminoethane; monoethylamine
- Appearance and odor: Colorless liquid or gas with a strong, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylamine is 10 parts of ethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 18 milligrams of ethylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylamine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Ethylamine causes severe irritation of the eyes and skin. It may also cause irritation of the nose, throat, and lungs.

2. Long-term Exposure: Repeated or prolonged exposure to ethylamine may also cause irritation of the lungs and kidney damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethylamine exposure.

—Chronic respiratory disease: Ethylamine causes lung irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethylamine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Ethylamine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Ethylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethylamine is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although ethylamine is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: Ethylamine causes myocardial degeneration in animals. Persons with cardiac disease may be at increased risk.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethylamine vapor is a primary irritant to mucous membranes, eyes, and skin. Exposure to 8000 ppm for 4 hours was lethal to rats. Rabbits survived exposures to

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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50 ppm daily for 6 weeks but showed pulmonary irritation and some myocardial degeneration; corneal damage was observed after 2 weeks of exposure. In the rabbit eye, 1 drop of a 70% solution of ethylamine caused immediate, severe irritation. Eye irritation and corneal edema in humans have been reported from industrial exposure. A 70% solution of the base dropped on the skin of guinea pigs caused prompt skin burns leading to necrosis; when held in contact with guinea pig skin for 24 hours there was severe skin irritation with extensive necrosis and deep scarring.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 45.1
2. Boiling point (760 mm Hg): 16.7 C (62 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of ethylamine): 1.6
5. Melting point: −81 C (−114 F)
6. Vapor pressure at 20 C (68 F): 1.18 atmospheres
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid ethylamine with strong acids will cause violent spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving ethylamine.
4. Special precautions: Liquid ethylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −18 C (less than 0 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Lower: 3.5; Upper: 14.0
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative data are available concerning the odor threshold of ethylamine.
2. Eye Irritation Level: Patty and the *Documentation of TLV's* report that in repeated exposure experiments, "100 ppm ethylamine produced irritation of the cornea" in rabbits. In addition, corneal injury, which did not appear for 2 weeks, was produced in rabbits exposed repeatedly to 50 ppm ethylamine. This concentration (50 ppm) is not specifically stated to be the lowest concentration producing eye injury.
3. Other Information: Patty and the *Documentation of TLV's* report that rabbits exposed to both 100 ppm and 50 ppm ethylamine for 7 hours per day, 5 days per week for 6 weeks, experienced lung irritation.
4. Evaluation of Warning Properties: Since no information is available concerning the odor threshold of ethylamine, and since the irritant effects produced by this substance are not stated to occur immediately upon exposure, ethylamine is treated as a substance with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethylamine in an adsorption tube containing silica gel, followed by desorption with sulfuric acid and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethylamine may be used. An analytical method for ethylamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid ethylamine, where skin contact may occur.

- Clothing wet with liquid ethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethylamine, the person performing the operation should be informed of ethylamine's hazardous properties.
- Where exposure of an employee's body to liquid ethylamine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with ethylamine should be removed immediately and not reworn until the ethylamine is removed from the clothing.
- Any clothing which becomes wet with liquid ethylamine should be removed immediately and not reworn until the ethylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid ethylamine or solutions containing ethylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid ethylamine or solutions containing 0.75% or more of ethylamine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with ethylamine should be immediately washed or showered to remove any ethylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of agricultural chemicals for herbicides; use as a dyestuff intermediate; use as a solvent for dyes, resins, and oils; use as a catalyst for polyurethane foams; use in pharmaceuticals, emulsifying agents, and as a vulcanization accelerator for sulfur-cured rubbers	General dilution ventilation; local exhaust ventilation
Use as a stabilizer for rubber latex; use as a catalyst for curing epoxy resins	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthesis of dimethylolethyltriazone, a wash and wear agent for cotton fabrics; synthesis of 1,3-diethylthiourea, a corrosion inhibitor	General dilution ventilation; local exhaust ventilation
Use in synthesis of chemical intermediates and solvents; use as plasticizers and in refining of lubricating oils	General dilution ventilation; local exhaust ventilation
Use as a selective solvent in refining of petroleum and vegetable oils	General dilution ventilation
Use in synthesis of alkyl isocyanates for intermediates in manufacture of organic products such as pharmaceuticals and resins	General dilution ventilation; local exhaust ventilation
Use in synthesis of rhodamine dyes	General dilution ventilation; local exhaust ventilation
Use as a deflocculating agent in ceramics industry; use in manufacture of detergents	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethylamine or solutions containing ethylamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethylamine gets on the skin, immediately flush the contaminated skin with water. If ethylamine soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethylamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Allow ethylamine to evaporate. Ethylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethylamine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR ETHYLAMINE

Condition	**Minimum Respiratory Protection* Required Above 10 ppm**
Gas Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
4000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against ethylamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Benzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5C_6H_5$
- Synonyms: Phenylethane; ethylbenzol
- Appearance and odor: Colorless liquid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl benzene is 100 parts of ethyl benzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 435 milligrams of ethyl benzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl benzene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Ethyl benzene causes irritation of the eyes, nose, throat, and skin. With exposure to high concentrations, irritating effects are more pronounced, and a person may begin to feel weak, dizzy, drowsy, and become unconscious.
2. *Long-term Exposure:* Prolonged or repeated ethyl benzene exposure of the skin may casue skin rash.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl benzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl benzene at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl benzene exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl benzene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Kidney disease: Although ethyl benzene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although ethyl benzene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: Ethyl benzene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl benzene is primarily an irritant of skin and, to some degree, of eyes and upper respiratory tract. Systemic absorption causes depression of the central nervous system with narcosis at very high concentrations. Aspiration of small amounts causes extensive edema and hemorrhage of lung tissue. It is readily metabolized and excreted chiefly as mandelic acid in the urine.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 106
  2. Boiling point (760 mm Hg): 136 C (277 F)
  3. Specific gravity (water = 1): 0.865
  4. Vapor density (air = 1 at boiling point of ethyl benzene): 3.66
  5. Melting point: −95 C (−139 F)
  6. Vapor pressure at 20 C (68 F): 7.1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
  8. Evaporation rate (butyl acetate = 1): Less than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl benzene.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 15 C (59 F) (closed cup)
  2. Autoignition temperature: 432 C (810 F)
  3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 6.7
  4. Extinguishant: Dry chemical, foam, or carbon dioxide
- **Warning properties**
  1. Odor Threshold: According to the Department of Transportation's *CHRIS Hazardous Chemical Data,*, ethyl benzene has an odor threshold of 140 ppm.
  2. Eye Irritation Level: According to the AIHA *Hygienic Guide*, "the vapor caused a noticeable eye irritation in humans at concentrations of 200 ppm."
  3. Evaluation of Warning Properties: Through its odor and irritant effects, ethyl benzene can be detected at a concentration less than twice the permissible exposure limit. Therefore, for the purposes of this guideline, ethyl benzene is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl benzene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl benzene may be used. An analytical method for ethyl benzene is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl benzene.
- Clothing wet with liquid ethyl benzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl benzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl benzene, the person performing the operation should be informed of ethyl benzene's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid ethyl benzene should be removed promptly and not reworn until the ethyl benzene is removed from the clothing.
- Any clothing which becomes wet with liquid ethyl benzene should be removed immediately and not reworn until the ethyl benzene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl benzene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid ethyl benzene should be promptly washed or showered with soap or mild detergent and water to remove any ethyl benzene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl benzene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of styrene monomer	Local exhaust ventilation
Use during spray application of vinyl resin surface coating	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of paints, varnishes, and other surface coatings	Local exhaust ventilation; general dilution ventilation
Use in manufacture and application of rubber adhesives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during electroplating of aluminum on copper or steel	Local exhaust ventilation for open-surface tanks
Liberation during oven baking and drying of surface coatings	Local exhaust ventilation for ovens
Liberation during application of surface coatings by dipping, flow coatings, and roller coating	Local exhaust ventilation
Liberation during use as an intermediate in dye manufacture	General dilution ventilation
Use as a heat-transfer medium; use as a dielectric	General dilution ventilation; personal protective equipment
Liberation during production of acetophenone by oxidation of ethyl benzene	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl benzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl benzene gets on the skin, promptly flush the contaminated skin with water. If ethyl benzene soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl benzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If ethyl benzene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl benzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid. Ethyl benzene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Ethyl benzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

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RESPIRATORY PROTECTION FOR ETHYL BENZENE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Bromide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_2H_5Br
- Synonyms: Bromoethane
- Appearance and odor: Colorless to yellow liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl bromide is 200 parts of ethyl bromide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 890 milligrams of ethyl bromide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl bromide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to ethyl bromide may cause irritation of the lungs, eyes, and skin. It may cause dizziness, loss of balance, slurred speech, unconsciousness, and death. Overexposure to this agent may also cause damage to the liver, kidneys, and heart. After-effects from severe exposure may occur up to 30 hours after the exposure has ceased.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl bromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl bromide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl bromide exposure.

—Skin disease: Ethyl bromide can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Ethyl bromide has produced liver damage in animals and man, which should be considered before exposing persons with impaired liver function.

—Kidney disease: Since ethyl bromide has produced kidney damage in animals and man, special consideration in those with impaired renal function is justified.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl bromide might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of ethyl bromide might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl bromide vapor is a respiratory irritant, a narcotic, and a hepato- and renal toxin. Exposure of guinea pigs for 30 minutes to 2.4% by volume (24,000 ppm) was fatal within 3 days due to pulmonary congestion, centrolobular necrosis of the liver, and diffuse nephritis; exposure to 3200 ppm for 9 hours produced lung irritation and nephritis; death occurred after 1 to 5 days.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

The former use of ethyl bromide as a human anesthetic produced respiratory irritation and caused some fatalities, either immediately, due to respiratory or cardiac arrest, or delayed, from effects on the liver, kidney, or heart. Relatively little experience with this substance in industry has been reported, but exposure of volunteers to 6500 ppm for 5 minutes produced vertigo, slight headache, and mild eye irritation. Irritation of the skin occurs from repeated contact with ethyl bromide liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 109
2. Boiling point (760 mm Hg): 38.8 C (100 F)
3. Specific gravity (water = 1): 1.45
4. Vapor density (air = 1 at boiling point of ethyl bromide): 3.8
5. Melting point: −119 C (−182 F)
6. Vapor pressure at 20 C (68 F): 375 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.9
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl bromide. Ethyl bromide readily decomposes into hydrogen bromide and bromine particularly in the presence of hot surfaces.
4. Special precautions: Liquid ethyl bromide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −20 C (less than −4F) (closed cup)
2. Autoignition temperature: 511 C (952 F)
3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 11.3
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Since the AIHA *Hygienic Guide* states that the odor of ethyl bromide is detectable only at concentrations well above the permissible exposure, it has been treated as a substance with poor warning properties. In addition, the *Hygienic Guide* reports a situation in which only mild eye irritation was produced in a human subject after a 5-minute exposure to 6500 ppm, a concentration many times greater than the permissible exposure. Information on the eye irritation threshold is not available.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl bromide vapors using an adsorption tube with subsequent desorption with isopropyl alcohol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl bromide may be used. An analytical method for ethyl bromide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl bromide.

- Clothing contaminated with liquid ethyl bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl bromide, the person performing the operation should be informed of ethyl bromide's hazardous properties.
- Any clothing which becomes wet with liquid ethyl bromide should be removed immediately and not reworn until the ethyl bromide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl bromide may contact the eyes.

SANITATION

- Skin that becomes wet with liquid ethyl bromide should be promptly washed or showered with soap or mild detergent and water to remove any ethyl bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use as an alkylating or ethylating agent in manufacture of pharmaceuticals, and to a lesser extent, chemicals, dyes, and perfumes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for fats, waxes, and resins	Process enclosure; if possible, local exhaust ventilation; personal protective equipment
Use as a local surface anesthetic for minor surgery and neuralgic pain	General dilution ventilation
Use as a liquid fumigant for grain and fruit	General dilution ventilation; personal protective equipment
Liberation during use as a refrigerant	Process enclosure; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl bromide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl bromide gets on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If ethyl bromide soaks through the clothing, remove the clothing promptly and flush the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl bromide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl bromide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl bromide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Ethyl bromide should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

Sewers designed to preclude the formation of explosive concentrations of ethyl bromide vapors are permitted.

- Waste disposal method:

Ethyl bromide may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethyl Bromide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Ethyl Bromide," *Hygienic Guide Series*, Detroit, Michigan, 1965.
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RESPIRATORY PROTECTION FOR ETHYL BROMIDE

Condition	**Minimum Respiratory Protection* Required Above 200 ppm**
Vapor Concentration	
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 3500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Butyl Ketone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5COC_4H_9$
- Synonyms: Butyl ethyl ketone; 3-heptanone
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl butyl ketone is 50 parts of ethyl butyl ketone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 230 milligrams of ethyl butyl ketone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl butyl ketone can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Ethyl butyl ketone may cause irritation of the eyes, nose, throat, and lungs. Exposure to high concentrations may cause headaches, dizziness, or unconsciousness.

2. Long-term Exposure: Prolonged or repeated skin contact may cause dryness and irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl butyl ketone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl butyl ketone at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl butyl ketone exposure.

—Kidney disease: Although ethyl butyl ketone is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl butyl ketone might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although ethyl butyl ketone is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: Ethyl butyl ketone is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

There is some local irritation of the skin and respiratory tract by solvent effect of ethyl butyl ketone on lipids. Central nervous depression occurs on exposure to high concentration, producing narcosis. Effects may be more pronounced in unacclimated individuals. No chronic systemic effects have been reported.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 114
  2. Boiling point (760 mm Hg): 147 C (297 F)
  3. Specific gravity (water = 1): 0.82
  4. Vapor density (air = 1 at boiling point of ethyl butyl ketone): 3.93
  5. Melting point: −39 C (−38 F)
  6. Vapor pressure at 20 C (68 F): 4 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.43
  8. Evaporation rate (butyl acetate = 1): 0.45
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl butyl ketone.
  4. Special precautions: Ethyl butyl ketone will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 46 C (115 F) (open cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: 1.4; Upper: 8.8
  4. Extinguishant: Carbon dioxide, dry chemical, or foam
- **Warning properties**
  1. Odor Threshold: According to Patty, ethyl butyl ketone has a "typical ketone-type odor."
  2. Eye Irritation Level: According to the *Documentation of TLV's*, "when in contact with skin and eyes, it (ethyl butyl ketone) produces, at most, irritation of mild degree."
  3. Evaluation of Warning Properties: For the purposes of this guideline, ethyl butyl ketone is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl butyl ketone vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl butyl ketone may be used. An analytical method for ethyl butyl ketone is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl butyl ketone.
- Clothing wet with liquid ethyl butyl ketone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl butyl ketone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl butyl ketone, the person performing the operation should be informed of ethyl butyl ketone's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid ethyl butyl ketone should be removed promptly and not reworn until the ethyl butyl ketone is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl butyl ketone may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid ethyl butyl ketone should be promptly washed or showered to remove any ethyl butyl ketone.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl butyl ketone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during application of lacquers, varnishes, epoxies, vinyl coatings, finishes, and adhesives	Local exhaust ventilation; personal protective equipment
Liberation during application of lacquer, varnishes, epoxies, vinyl coatings, finishes, and adhesives by dipping, roller coating, tumbling, knifing, or brushing	Local exhaust ventilation; general dilution ventilation
Liberation during oven or air drying of coatings and adhesives	General dilution ventilation
Use during manual application of cellulosic, acetate, and rubber adhesives in shoe manufacturing, book binding, and packaging	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of cellulosic household cements	General dilution ventilation
Liberation during application of mastics or other natural gum/ based adhesives for floor and wall tiles, other floor coverings, automobile silencer, and lining pads	General dilution ventilation; local exhaust ventilation
Liberation during cleaning and maintenance of ketone-processing equipment, such as distillation columns, reactors, mixers, and storage vessels	Personal protective equipment
Liberation during blending of coating and adhesive raw materials in open mixers	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl butyl ketone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl butyl ketone gets on the skin, promptly flush the contaminated skin with water. If ethyl butyl ketone soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is evidence of skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl butyl ketone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl butyl ketone has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl butyl ketone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Ethyl butyl ketone should not be

allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of ethyl butyl ketone vapors are permitted.

- Waste disposal methods:

Ethyl butyl ketone may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHYL BUTYL KETONE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, a full-facepiece respirator should be worn.

Occupational Health Guideline for Ethyl Chloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_2H_5Cl
- Synonyms: Chloroethane; monochloroethane; hydrochloric ether; muriatic ether
- Appearance and odor: Colorless liquid or gas with a pungent, ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl chloride is 1000 parts of ethyl chloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2600 milligrams of ethyl chloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl chloride can affect the body if it is inhaled, if it comes in contact with the eyes or skin. or if it is swallowed. In the liquid form, it may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Ethyl chloride may cause drowsiness, unconsciousness, irregular heart beat, and death. It may also cause irritation of the eyes and abdominal cramps. Spilled on the skin, it may cause frostbite.

2. Long-term Exposure: Ethyl chloride may cause liver and kidney damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl chloride at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl chloride exposure.

—Liver disease: Ethyl chloride is known as a liver toxin in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Ethyl chloride is known as a kidney toxin in animals and justifies special consideration before exposing persons with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl chloride might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of ethyl chloride might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl chloride vapor is a narcotic. Guinea pigs died from a 9-hour exposure to 40,000 ppm but survived 4-½ hour exposure; histopathological changes in the lungs, liver, and kidneys were observed in animals in the latter group. Inhalation of 40,000 ppm by human subjects caused dizziness, eye irritation, and abdominal cramps, while inhalation of 3.36% by volume (33,600 ppm) caused a toxic effect after 30 seconds, increasing within 5 minutes to noisy talkativeness followed by incoordina-

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tion. At 2.5% by volume (25,000 ppm) there was incoordination; 1.9% (19,000 ppm) caused weak analgesia after 12 minutes, and 1.3% (13,000 ppm) caused slight symptoms of inebriation. Sudden and unforeseen fatalities from ethyl chloride anesthesia have been reported, probably due to respiratory or cardiac arrest. Chronic effects from industrial exposure have not been reported, although skin absorption is said to occur. In liquid form this substance may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 64.5
2. Boiling point (760 mm Hg): 12.2 C (54 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of ethyl chloride): 2.2
5. Melting point: −139 C (−218 F)
6. Vapor pressure at 20 C (68 F): 1064 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.57
8. Evaporation rate (butyl acetate = 1): Much higher than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving ethyl chloride.
4. Special precautions: Liquid ethyl chloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −50 C (−58 F) (closed cup)
2. Autoignition temperature: 519 C (966 F)
3. Flammable limits in air, % by volume: Lower: 3.8; Upper: 15.4
4. Extinguishant: Stop flow of gas. Use carbon dioxide, dry chemical, or foam for small fires.

- **Warning properties**

Ethyl chloride has a somewhat pungent, ether-like odor, but no quantitative data are available on the odor threshold. For the purposes of this guideline, therefore, ethyl chloride has been treated as a material with poor warning properties.

Ethyl chloride is a mild eye irritant. Grant reports that at 4% the gas has been noted to cause slight irritation of the eyes of human beings.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for ethyl chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl chloride.
- Clothing wet with liquid ethyl chloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl chloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl chloride, the person performing the operation should be informed of ethyl chloride's hazardous properties.
- Any clothing which becomes wet with liquid ethyl chloride should be removed immediately and not reworn until the ethyl chloride has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl chloride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of tetraethyl lead and ethyl cellulose	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a local or general anesthetic; use as a refrigeration compound; use as a solvent for fats, oils, waxes, phosphorus, acetylene, and many resins	General dilution ventilation; personal protective equipment
Use in organic synthesis of perchloroethane, esters, and Grignard reagents	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of dyes and drugs; use as a propellant in aerosols	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of perfumes	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid ethyl chloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid ethyl chloride gets on the skin, promptly wash the contaminated skin with water if the ethyl chloride has not already evaporated. If liquid ethyl chloride soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl chloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl chloride has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Ethyl chloride should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
4. If in the gaseous form, stop flow of gas.

- Waste disposal methods:

Ethyl chloride may be disposed of:

1. If in the liquid form, by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. If in the gaseous form, by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR ETHYL CHLORIDE

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
20,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethylene Chlorohydrin

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2ClCH_2OH
- Synonyms: 2-Chloroethanol; 2-chloroethyl alcohol
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylene chlorohydrin is 5 parts of ethylene chlorohydrin per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 16 milligrams of ethylene chlorohydrin per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for ethylene chlorohydrin a Threshold Limit Value of 1 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylene chlorohydrin can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may be absorbed through the skin without causing irritation.

- **Effects of overexposure**

Exposure to ethylene chlorohydrin vapor may cause irritation of the eyes, nose, throat, and lungs, nausea, vomiting, dizziness, poor coordination, numbness, visual disturbance, liver or kidney damage (lower concentrations may cause serious effects without causing irritation). Breathing in higher concentrations produces headache, thirst, delirium, low blood pressure, collapse, and unconsciousness. The urine may contain blood. Death may occur from lung or brain damage. Absorption through the skin can cause the above symptoms without skin irritation. Prolonged overexposure to ethylene chlorohydrin may cause the skin to become yellow and a change in frequency of urination or the amount of urine.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethylene chlorohydrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylene chlorohydrin at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, liver, kidneys, and central nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Ethylene chlorohydrin may cause liver damage. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on a semi-annual basis for the first two years and annually thereafter.

- **Summary of toxicology**

Ethylene chlorohydrin vapor is highly toxic to the liver, kidneys, brain, and other organs. It is rapidly absorbed through the skin. A concentration of 250 ppm was fatal to rats in 4 hours; 125 ppm was not. A human fatality was reported following exposure to an estimat-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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ed 300 ppm for 2-¼ hours. In another fatal case, autopsy showed severe damage to the liver and brain. Several employees survived exposures averaging 18 ppm but showed signs of circulatory shock with incoordination and repeated vomiting. There is little margin of safety between early reversible symptoms and fatal intoxication. Absorption by any route, including the skin, may lead to severe illness or death. Contact with vapor causes irritation of mucous membranes, nausea, vomiting, vertigo, incoordination, numbness, and visual disturbance. With higher concentrations, headache, severe thirst, delirium, low blood pressure, collapse, shock, and coma may result. Urine may contain albumin, casts, and red blood cells. Death results from pulmonary edema or from congestion and edema of the brain. The cause of the toxic effect is probably the result of oxidation of the alcohol to chloracetic acid. The liquid instilled in rabbit eyes caused moderately severe injury, but in human eyes corneal burns have been observed to recover within 48 hours. Skin contact is particularly hazardous, because there are no signs of immediate irritation to warn the victim of exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 80.5
2. Boiling point (760 mm Hg): 130 C (266 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of ethylene chlorohydrin): 2.8
5. Melting point: −62.6 C (−81 F)
6. Vapor pressure at 20 C (68 F): 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong caustics may cause formation of flammable ethylene gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving ethylene chlorohydrin.
4. Special precautions: Ethylene chlorohydrin will attack some forms of plastics, rubber, and coatings. Special attention to the care and maintenance of personal protective equipment should be maintained.

- **Flammability**

1. Flash point: 60 C (140 F) (closed cup)
2. Autoignition temperature: 425 C (797 F)
3. Flammable limits in air, % by volume: Lower: 4.9; Upper: 15.9
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

According to the AIHA *Hygienic Guide*, the warning properties of ethylene chlorohydrin are "poor and inadequate to prevent injury."

Ethylene chlorohydrin is an eye irritant, according to the *Hygienic Guide*.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethylene chlorohydrin vapors using an adsorption tube with subsequent desorption with isopropyl alcohol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethylene chlorohydrin may be used. An analytical method for ethylene chlorohydrin is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with ethylene chlorohydrin.

- Clothing contaminated with liquid ethylene chlorohydrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylene chlorohydrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethylene chlorohydrin, the person performing the operation should be informed of ethylene chlorohydrin's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid ethylene chlorohydrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid ethylene chlorohydrin should be removed immediately and not reworn until the ethylene chlorohydrin is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid ethylene chlorohydrin contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid ethylene chlorohydrin, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid ethylene chlorohydrin should be immediately washed or showered to remove any ethylene chlorohydrin.
- Eating and smoking should not be permitted in areas where liquid ethylene chlorohydrin is handled, processed, or stored.
- Employees who handle liquid ethylene chlorohydrin should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethylene chlorohydrin may occur and control methods which may be effective in each case:

Operation	Controls
Use as a fumigant in treatment of seed potatoes	General dilution ventilation; personal protective equipment
Use in dyeing operations during color printing of textiles	Process enclosure; local exhaust ventilation
Use during cleaning, degreasing, and dewaxing operations	Material substitution; process enclosure; local exhaust ventilation
Use in organic synthesis and synthesis of dyes, pharmaceuticals, and resin processing; use in extraction of pine lignin and oil of rose	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethylene chlorohydrin gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethylene chlorohydrin gets on the skin, immediately flush the contaminated skin with water. If ethylene chlorohydrin soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of ethylene chlorohydrin, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethylene chlorohydrin has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If ethylene chlorohydrin is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Ethylene chlorohydrin should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Ethylene chlorohydrin may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethylene Chlorohydrin," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR ETHYLENE CHLOROHYDRIN

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
10 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ethylene chlorohydrin; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethylenediamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $NH_2CH_2CH_2NH_2$
- Synonyms: 1,2-Diaminoethane; ethylenediamine, anhydrous; 1,2-ethanediamine
- Appearance and odor: Colorless liquid or solid with an ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylenediamine is 10 parts of ethylenediamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of ethylenediamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylenediamine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Ethylenediamine vapors may cause irritation of the eyes, nose, and throat. If splashed on the skin, it may cause severe irritation, skin damage, and blistering. If splashed in the eyes, it may cause damage. It may cause tingling of the face.

2. Long-term Exposure: Repeated or prolonged overexposure to ethylenediamine may cause dermatitis. A person may become allergic to ethylenediamine (skin rash and asthma). Liver, kidney, and lung damage may occur from repeated exposure to this chemical.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethylenediamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylenediamine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to ethylenediamine would be expected to be at increased risk from exposure. Examination of the respiratory system, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Ethylenediamine vapor is a sensitizer and primary irritant to the skin, mucous membranes, and respiratory tract. Exposure of rats to 4000 ppm for 8 hours was uniformly fatal as a result of kidney injury, although some lung injury also occurred; 2000 ppm was not lethal. Rats exposed daily for 30 days to 484 ppm did not survive; injury to lungs, liver, and kidneys was observed; at 132 ppm there was no mortality. In human subjects, inhalation of 400 ppm for 5 to 10 seconds caused intolerable nasal irritation; 200 ppm caused tingling of the face and slight nasal irritation; 100 ppm was not irritating. In the eye of a rabbit the liquid caused extreme irritation and corneal damage; partial corneal opacity was produced by a 5% solution. The undiluted liquid applied to the shaved skin of rabbits and left uncovered produced severe irritation and ne-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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crosis. Cutaneous sensitization in man has been observed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60.1
2. Boiling point (760 mm Hg): 117 C (242 F)
3. Specific gravity (water = 1): 0.91
4. Vapor density (air = 1 at boiling point of ethylenediamine): 2.1
5. Melting point: 11 C (52 F)
6. Vapor pressure at 20 C (68 F): 10 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 0.91

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid ethylenediamine with strong acids will cause violent spattering. Contact with strong oxidizers and chlorinated organic compounds may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving ethylenediamine.
4. Special precautions: Liquid ethylenediamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 34 C (93 F) (closed cup)
2. Autoignition temperature: 379.4 C (715 F)
3. Flammable limits in air, % by volume: Lower: 5.8; Upper: 11.1
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that the ammonia-like odor of ethylenediamine is detectable at 10 ppm.
2. Eye Irritation Level: Grant notes that "workmen exposed to ethylenediamine are said occasionally to see haloes around objects and to have some blurring of vision, presumably attributable to an effect on the corneal epithelium." Grant does not give any quantitative information, however.

The *Hygienic Guide* reports that ethylenediamine vapor causes eye irritation, but the exact concentrations producing the irritation are not given. They also state that "a chemical cartridge respirator with a cartridge designed for amine vapors may be used for protection against concentrations of ethylenediamine that do not cause eye irritation."

3. Other Information: The *Documentation of TLV's* states that "human subjects found 100 ppm for a few seconds to be inoffensive, but higher concentrations, 200 and 400 ppm, produced noticeable irritation of the nasal mucosa."
4. Evaluation of Warning Properties: Since the odor of ethylenediamine is noticeable at the permissible exposure, this material is treated as a substance with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for ethylenediamine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid ethylenediamine.
- If employees' clothing has had any possibility of being contaminated with solid ethylenediamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with solid or liquid ethylenediamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylenediamine from the clothing. If the

clothing is to be laundered or otherwise cleaned to remove the ethylenediamine, the person performing the operation should be informed of ethylenediamine's hazardous properties.

- Where there is any possibility of exposure of an employee's body to solid or liquid ethylenediamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with liquid ethylenediamine or non-impervious clothing which becomes contaminated with ethylenediamine should be removed immediately and not reworn until the ethylenediamine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid ethylenediamine or solutions containing ethylenediamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid or solid ethylenediamine or solutions containing more than 5% ethylenediamine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with ethylenediamine should be immediately washed or showered to remove any ethylenediamine.
- Workers subject to skin contact with solid or liquid ethylenediamine should wash any areas of the body which may have contacted ethylenediamine at the end of each work day.
- Eating and smoking should not be permitted in areas where solid or liquid ethylenediamine are handled, processed, or stored.
- Employees who handle solid or liquid ethylenediamine should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethylenediamine may occur and control methods which may be effective in each case:

Operation	**Controls**
Use in manufacture of carbamate fungicides, pesticides, and weed killers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of chelating agents in dyes, soaps, and cleaning compounds, water treatment, in agriculture, in rubber processing, in pulp and paper processing, and in metal cleaning and electroplating	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of urea resins for use in textile and paper finishing; use in production of textile finishing compounds, resins, rubber products, insecticides, and medicinals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an activator for epoxy resin menders; in preparation of Spandex, adhesives, inks, surface coatings, cross-linking agents, plasticizers, resins curing compounds, and as a dye assist	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of surfactants, emulsifying agents, wetting agents, dispersants, corrosion inhibitors, detergents, and textile surface treatments	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for preparation of dye intermediates, heterocyclic compounds, pharmaceuticals, corrosion inhibitors, adhesives, and salts	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Miscellaneous uses in brightening agent for electroplating, anti-tarnish agent in detergents, lubricant stabilizer, soldering fluxes, processing chemicals for rubber, solvent for casein, albumin, shellac, and sulfur	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid or liquid ethylenediamine or solutions containing ethylenediamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid ethylenediamine gets on the skin, immediately flush the contaminated skin with water. If solid or liquid ethylenediamine penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethylenediamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethylenediamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethylenediamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the liquid form, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Ethylenediamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
4. If in the solid form, collect, allow to melt, and dispose of the liquid as above.

- Waste disposal method:

Ethylenediamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR ETHYLENEDIAMINE

Condition	**Minimum Respiratory Protection* Required Above 10 ppm**
Vapor Concentration	
500 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing *protection* against ethylenediamine. A gas mask with a chin-style or a front- or back-mounted canister providing protection against ethylenediamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
12000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood *operated in continuous-flow mode.*
Greater than 2000 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other *positive pressure mode.* A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against ethylenediamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from* airborne concentrations of ethylenediamine; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethylene Dibromide *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2BrCH_2Br
- Synonyms: 1,2-Dibromoethane; ethylene bromide
- Appearance and odor: Colorless liquid or solid with a mild, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylene dibromide is 20 parts of ethylene dibromide per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 30 ppm and a maximum peak of 50 ppm for 5 minutes during an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to a ceiling level of 1 mg/m^3 (0.13 ppm) averaged over a 15-minute period. The NIOSH Criteria Document for Ethylene Dibromide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylene dibromide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Ethylene dibromide may cause vomiting, irritation of the eyes, nose, throat, and skin. It may also cause drowsiness. In addition, overexposure may cause damage to the lungs, liver, and kidneys.
2. Long-term Exposure: Prolonged or repeated exposure to ethylene dibromide may cause injury to the lungs, liver, or kidneys. Adverse effects, including abnormalities in offspring, mutations, and stomach cancer, have been found in animals following exposure to ethylene dibromide. The relevance to humans of these findings has not yet been established.
3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethylene dibromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylene dibromide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the nervous and respiratory systems, heart, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ethylene dibromide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ethylene dibromide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Ethylene dibromide may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Although ethylene dibromide is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Skin disease: Ethylene dibromide is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Medical warning: Workers should be informed that adverse effects have been found in animals following exposure to ethylene dibromide. These effects have included abnormalities in offspring, mutations, and stomach cancer.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Ethylene dibromide vapor is a narcotic, a severe mucous membrane irritant, and a hepatic toxin. Rats did not survive when exposed to the vapor for longer than 6 minutes at 3000 ppm; minimum lethal concentration for an 8-hour exposure was 200 ppm; these exposures caused hepatic necrosis, pulmonary edema, and cloudy swelling of renal tubules. Four species of animals tolerated daily inhalation of 25 ppm for 6 months without adverse effects but did not tolerate similar exposure to 50 ppm. Accidental use as a human anesthetic resulted in severe irritation of the conjunctiva and respiratory tract, followed by protracted vomiting and death. Excessive exposure may be expected to cause irritation of the eyes and respiratory tract. The liquid is highly irritating to human skin, causing marked erythema and vesiculation. Serious skin injury has been reported from contact with clothing and especially shoes wet with ethylene dibromide. In a bioassay conducted by the National Cancer Institute (NCI), ethylene dibromide was found carcinogenic to rats and mice when fed by gavage. The compound induced squamous cell carcinomas of the fore stomach in rats of both sexes, hepatocellular carcinomas in female rats, and hemangiosarcomas in male rats. In mice of both sexes, the compound induced squamous cell carcinomas of the fore stomach and alveolar/broncheolar adenomas. In NIOSH-sponsored research, laboratory rats exposed to 20 ppm ethylene dibromide by inhalation and also receiving a diet containing 0.05% disulfiram experienced exceedingly high mortality levels as well as a high incidence of tumors (including hemangiosarcomas of the liver, spleen, and kidney).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 187.9
2. Boiling point (760 mm Hg): 131 C (268 F)
3. Specific gravity (water = 1): 2.18
4. Vapor density (air = 1 at boiling point of ethylene dibromide): 6.5
5. Melting point: 10 C (50 F)
6. Vapor pressure at 20 C (68 F): 11 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.4
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat; ethylene dibromide slowly decomposes in the presence of light.
2. Incompatibilities: Ethylene dibromide reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, magnesium, liquid ammonia, and strong oxidizers.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, bromine, and carbon monoxide) may be released when ethylene dibromide decomposes.
4. Special precautions: Liquid ethylene dibromide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

According to the International Labour Office (ILO), the odor of ethylene dibromide is detectable at 10 ppm, well above the NIOSH recommended permissible exposure concentration. Therefore, it is treated as a material with poor warning properties.

Ethylene dibromide is an eye irritant, according to Stecher.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of ethylene dibromide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Level Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of ethylene dibromide. Each measurement should consist of a 5-minute sample or a series of consecutive samples totalling 5 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of ethylene dibromide vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethylene dibromide may be used. An analytical method for ethylene dibromide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethylene dibromide.
- Non-impervious clothing which becomes contaminated with liquid ethylene dibromide should be removed immediately and not reworn until the ethylene dibromide is removed from the clothing.
- Clothing contaminated with liquid ethylene dibromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylene dibromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethylene dibromide, the person performing the operation should be informed of ethylene dibromide's hazardous properties.
- Where exposure of an employee's body to liquid ethylene dibromide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethylene dibromide may contact the eyes.

SANITATION

- Skin that becomes contaminated with ethylene dibromide should be immediately washed or showered with soap or mild detergent and water to remove any ethylene dibromide.
- Employees who handle ethylene dibromide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where ethylene dibromide is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethylene dibromide may occur and control methods which may be effective in each case:

Operation	Controls
Use in fumigation operations in preplanting and on grains, fruits, and vegetables	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in production of antiknock fluids and fuels	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of water-proofing agents fire extinguishing agents, and gauge fluids during manufacture of measuring intruments	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis in production of dyes, pharmaceuticals, and ethylene oxide; use as a specialty solvent for resins, gums, and waxes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Liberation during production and handling of fumigant preparations	Local exhaust ventilation; general mechanical ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethylene dibromide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethylene dibromide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If ethylene dibromide soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethylene dibromide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethylene dibromide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethylene dibromide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the liquid form, collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.
3. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing ethylene dibromide should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal methods:

Ethylene dibromide may be disposed of:

1. If in the liquid form, by absorbing it in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill.
2. If in the solid form, by disposing in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR ETHYLENE DIBROMIDE

Condition	**Minimum Respiratory Protection* Required Above 20 ppm**
Vapor Concentration	
400 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 400 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ethylene dibromide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 400 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE DICHLORIDE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethylene dichloride for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2H_4Cl_2$
- **Structure:** $ClCH_2CH_2Cl$
- **Synonyms:** 1,2-Dichloroethane, dichloroethylene, ethane dichloride, ethylene chloride, glycol dichloride
- **Identifiers:** CAS 107-06-2; RTECS KI0525000; DOT 1184, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless, oily liquid with an odor like chloroform

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.96
2. Boiling point (at 760 mmHg): 83.4°C (182°F)
3. Specific gravity (water = 1): 1.253
4. Vapor density (air = 1 at boiling point of ethylene dichloride): 3.42
5. Melting point: -35.4°C (-31.7°F)
6. Vapor pressure at 20°C (68°F): 68 mm Hg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.81
8. Evaporation rate (butyl acetate = 1): 6.46
9. Saturation concentration in air (approximate) at 25°C (77°F): 11.5% (115,000 ppm)
10. Ionization potential: 11.04 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizers, strong caustics, or chemically active metals such as aluminum or magnesium powder, sodium, or potassium may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving ethylene dichloride.
3. Caution: Ethylene dichloride is corrosive to iron and other metals unless it is stabilizied with alkylamines. Ethylene dichloride will attack some forms of plastics and rubber.

- **Flammability**

1. Flash point: 13°C (55°F) (closed cup)
2. Autoignition temperature: 413°C (775°F)
3. Flammable limits in air, % by volume: Lower, 6.2; Upper, 15.9
4. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 88 ppm
2. Eye irritation levels: 10 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ethylene dichloride is 50 parts of ethylene dichloride per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 100 ppm; and the maximum peak concentration above the acceptable ceiling concentration (maximum duration of 5 minutes in any 3 hours) is 200 ppm. The National Institute for Occupational Safety and Health (NIOSH) recommends that ethylene dichloride be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 1 ppm [4 milligrams of ethylene dichloride per cubic meter of air (mg/m^3)] as a TWA for up to a 10-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 2 ppm (8 mg/m^3) as determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 10 ppm

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($40\ mg/m^3$) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethylene dichloride

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	50	—
Acceptable ceiling	100	—
Maximum ceiling (5 min in any 3 h)	200	—
NIOSH REL TWA (Ca)*	1	4
Ceiling (15 min)	2	8
ACGIH TLV® TWA	10	40

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Ethylene dichloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Chronic inhalation or ingestion of ethylene dichloride by rats caused pulmonary tissue irritation, congestion, edema and pneumonia, degeneration of liver and kidney tissue, adrenal gland hemorrhage and cell damage, fatty infiltration and hemorrhage of cardiac tissue, and death due to respiratory or cardiac arrest. Cancers of the stomach, circulatory system, mammary glands, uterus, lungs, and skin were produced in similarly exposed rats and mice.

2. *Effects on humans:* Acute inhalation exposure to ethylene dichloride has caused respiratory tract irritation, congestion, edema and pneumonia, impaired functioning of the liver and kidneys, and myocardial hemorrhage. Chronic exposure has produced enlargement and fatty degeneration of the liver, impaired liver and kidney function, depression of nerve conduction, anemia, and increased serum bile salt levels. Ethylene dichloride has been detected in the milk of exposed lactating mothers.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to ethylene dichloride can cause headache, weakness, pain or irritation of the eyes and skin, bluish discoloration of skin and mucous membranes (cyanosis), nausea, vomiting, mental confusion, dizziness, incoordination, and unconsciousness.

2. *Long-term (chronic):* Exposure to ethylene dichloride can cause headache, fatigue, irritability, nervousness, cough, weakness, diarrhea, and muscle tremor. Severe irritation of the skin, edema, and tissue destruction (necrosis) can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to ethylene dichloride, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and reproductive, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to ethylene dichloride at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to ethylene dichloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and reproductive, cardiovascular, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to ethylene dichloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: None recognized (however, toxic hepatitis is a recognized SHE associated with occupational exposure to ethylene dibromide).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to ethylene dichloride should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of ethylene dichloride. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis for ethylene dichloride may be performed by collecting ethylene dichloride vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure ethylene dichloride may also be used if available. A detailed sampling and analytical method for ethylene dichloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1003).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with ethylene dichloride.

SANITATION

Clothing which is contaminated with ethylene dichloride should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of ethylene dichloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethylene dichloride's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with ethylene dichloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle ethylene dichloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethylene dichloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for ethylene dichloride

Operations	Controls
During use as a chemical intermediate in the manufacture of vinyl chloride	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an intermediate in the production of chlorinated solvents and ethyleneamines	Process enclosure, local exhaust ventilation, personal protective equipment
During the production of gasoline using tetraethyl lead as an anti-knock agent and ethylene dichloride as a lead scavenger	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a fumigant or industrial solvent	Local exhaust ventilation, personal protective equipment
During the manufacture of ethylene dichloride	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to ethylene dichloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethylene dichloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to ethylene dichloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethylene dichloride gets on the skin, wash it immediately with soap and water. If ethylene dichloride penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If ethylene dichloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing ethylene dichloride, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing ethylene dichloride may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing ethylene dichloride may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for ethylene dichloride

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE GLYCOL

INTRODUCTION

This guideline summarizes pertinent information about ethylene glycol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_2H_6O_2$

- **Structure**

  CH_2OHCH_2OH

- **Synonyms**

  1,2-Dihydroxyethane; 1,2-ethanediol; 2-hydroxyethanol; ethane-1,2-diol; ethylene alcohol; ethylene dihydrate; glycol; monoethylene glycol; glycol alcohol; Lutrol-9; Macrogol 400BPC; Norkool; Dowtherm SR 1

- **Identifiers**

1. CAS No.: 107-21-1
2. RTECS No.: KW2975000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

  Ethylene glycol is a combustible, slightly viscous, colorless liquid with a sweet taste and no odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 62.1
2. Boiling point (760 mm Hg): 197.6°C (387.7°F)
3. Specific gravity (water = 1): 1.11 at 20°C (68°F)
4. Vapor density: 2.1
5. Melting/freezing point: -13°C (8.6°F)
6. Vapor pressure at 20°C (68°F): 0.06 mm Hg
7. Solubility: Miscible in water, ethanol, glycerol, acetic acid, and acetone; slightly soluble in ether; practically insoluble in benzene and its homologs, chlorinated hydrocarbons, petroleum ether, and oils.
8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. Ethylene glycol that is heated or misted into the air presents a moderate fire and explosion hazard.
2. Incompatibilities: Ethylene glycol can react dangerously with chlorosulfonic acid, oleum, sulfuric acid, and strong oxidizing agents such as perchlorates, peroxides, permanganates, chlorates, and nitrates.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving ethylene glycol.
4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to ethylene glycol.

1. Flash point: 115°C (240°F) (open cup); 111°C (232°F) (closed cup)
2. Autoignition temperature: 398°C (748°F)
3. Flammable limits in air (percent by volume): Lower, 3.2; upper, data not available
4. Extinguishant: Use water spray, dry chemical, "alcohol" foam, or carbon dioxide to fight fires involving ethylene glycol. Water or foam may cause frothing. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to dilute spills to noncombustible mixtures.

Fires involving ethylene glycol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of ethylene glycol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethylene glycol. Structural firefighters' protective clothing may provide limited protection against fires involving ethylene glycol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethylene glycol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for ethylene glycol [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) assigns ethylene glycol a ceiling limit value of 50 ppm (127 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of respiratory tract irritation associated with exposure to ethylene glycol [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ethylene glycol can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to airborne concentrations of ethylene glycol causes eye and upper respi-

ratory tract irritation, and ingestion causes central nervous system depression, kidney and liver injury, and fetotoxic and developmental effects in experimental animals. In contact with the eyes or skin of rabbits, ethylene glycol caused irritation classified as mild [NIOSH 1994]. The dermal LD_{50} in rabbits is 9,530 mg/kg [NIOSH 1994]. The oral LD_{50} is 4,700 mg/kg in rats, 5,500 mg/kg in mice, and 6,610 mg/kg in guinea pigs [NIOSH 1994]. Dogs and cats given oral doses of ethylene glycol developed ataxia, vomiting, polydipsia, and seizures before losing consciousness [NLM 1993]. Exposure to a 12-mg/m^3 concentration of ethylene glycol continuously for 90 days, however, caused a moderate to severe degree of eye irritation in rabbits and rats [ACGIH 1991]. Dietary levels of ethylene glycol as high as 2 percent for 2 years caused decreased life span, calcium oxalate bladder stones, and kidney and liver damage in rats; the no-effect level in this study was no more than 0.2 percent in the diet (100 mg/kg/day) for 2 years [Clayton and Clayton 1981]. Several studies in rats and mice given oral doses of ethylene glycol during pregnancy have shown fetotoxic and developmental effects [NIOSH 1994].

2. *Effects on Humans:* Exposure to ethylene glycol vapor or mist causes eye, nose, and upper respiratory tract irritation in humans. In one report, reversible conjunctival inflammation occurred after ethylene glycol was splashed into a worker's eye [Hathaway et al. 1991]. By ingestion or percutaneous absorption, ethylene glycol causes central nervous system effects, liver and kidney damage, and cardiopulmonary effects. Loss of consciousness and nystagmus were reported among 9 of 38 women exposed to ethylene glycol vapor, and 5 of these workers also showed lymphocytosis [Clayton and Clayton 1981]. Throat irritation, headache, and backache were reported in human volunteers exposed to a mean concentration of ethylene glycol mist ranging from 1.4 to 27 ppm for 20 to 22 hours/day for 4 weeks. At a concentration of 60 ppm, symptoms were common; at 80 ppm, coughing and a sensation of tracheal burning became intolerable [ACGIH 1991]. Ingestion of a large amount (100 ml or more) of ethylene glycol produces three well-documented stages of toxicity. In Stage 1, which occurs within 30 minutes, nausea and vomiting, slurred speech, ataxia, nystagmus, lethargy, and a faint, sweetish odor on the breath develop. Coma, convulsions, and respiratory depression or cardiovascular collapse also may occur at this stage. In Stage 2, cardiopulmonary effects progress and cyanosis, pulmonary edema, and congestive heart failure may develop. In Stage 3, acute tubular necrosis develops, with oxaluria or anuria; these signs may progress to uremia and renal failure [Clayton and Clayton 1981; Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute airborne exposure to ethylene glycol include redness and irritation of the eyes and eyelids, sore throat, runny nose, cough, headache, and backache. Massive ingestion causes nausea; vomiting; slurred speech; ataxia; nystagmus; lethargy; impaired vision; a faint, sweet odor on the breath; coma; convulsions; elevated body temperature; elevated heart and respiratory rates; hypotension; agitation; confusion; cyanosis; tremor; areflexia; muscle twitches or contractions; crystalluria; hematuria; proteinuria; oxaluria; anuria; uremia; and cardiopulmonary collapse.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to ethylene glycol have been reported in humans.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of ethylene glycol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if ethylene glycol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by touching the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ethylene glycol and lead to worker exposures to this substance:

—Use as antifreeze in cooling and heating systems

—Use as a vehicle for pharmaceutical preparations, food extracts, and flavoring essences and as a component of skin lotions, a substitute for glycerin, and an ingredient in various powders

—Use in electrolytic condensers as a solvent for boric acid and borates

—Use as a solvent in the paint and plastics industries

—Use in the formulation of printers' inks, stamp pad inks, and inks for ball point pens

—Use in the synthesis of safety explosives, glyoxal, unsaturated ester-type alkylated resins, plasticizers, elastomers, synthetic fibers (terylene and dacron), and synthetic waxes

—Use as an industrial humectant

The following methods are effective in controlling worker exposures to ethylene glycol, depending on the feasibility of implementation:

— Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to ethylene glycol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, upper respiratory tract, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ethylene glycol at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, upper respiratory tract, or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ethylene glycol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethylene glycol on the eyes, upper respiratory tract, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although several of the metabolites of ethylene glycol can be detected in body fluids (serum, urine, blood) of exposed individuals, levels of these metabolites do not correlate well with airborne concentrations of ethylene glycol. Therefore, no biological monitoring test acceptable for routine use has yet been developed for ethylene glycol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne ethylene glycol is made using a glass fiber filter in a Swinnex (TM) cassette, followed by a silica gel tube (520/260 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a minimum collection time of 5 minutes is reached. As soon as possible after sampling, the filter is removed from the cassette and placed in a vial with a Teflon-lined cap containing 1 mL of 2% isopropanol in water. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1993] and in Method No. 5500 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If ethylene glycol contacts the skin, workers should flush the affected areas with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with ethylene glycol should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of ethylene glycol, particularly its potential to be irritating to the eyes, nose, and upper respiratory tract.

A worker who handles ethylene glycol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where ethylene glycol or a solution containing ethylene glycol is handled, processed, or stored.

STORAGE

Ethylene glycol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Since some containers can affect the color of this material, resin-coated steel, glass, aluminum, or stainless steel containers should be used for storage. Containers of ethylene glycol should be protected from physical damage and should be stored separately from chlorosulfonic or sulfuric acid, oxidizing agents such as perchlorates, peroxides, permanganates, chlorates, nitrates, moisture, heat, sparks, and open flame. Because containers that formerly contained ethylene glycol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethylene glycol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the ethylene glycol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Ethylene glycol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of ethylene glycol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of ethylene glycol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of ethylene glycol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-

261.24. Although ethylene glycol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ethylene glycol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with ethylene glycol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against ethylene glycol and have demonstrated good-to-excellent resistance for periods of greater than 8 hr: natural rubber, butyl rubber, neoprene, polyvinyl chloride, nitrile rubber, polyethylene, Teflon, Viton, Saranex, and Barricade. 4H and Responder have demonstrated good-to-excellent resistance for periods of greater than 4 hr and less than 8 hr. Polyvinyl alcohol has a breakthrough time of 1 to 4 hr and should be used with caution against ethylene glycol.

If ethylene glycol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ethylene glycol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ethylene glycol. Contact lenses should not be worn if the potential exists for ethylene glycol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR NITROGLYCERIN AND ETHYLENE GLYCOL DINITRATE

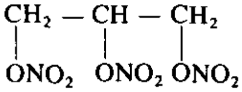
INTRODUCTION

This guideline summarizes pertinent information about nitroglycerin (NG) and ethylene glycol dinitrate (EGDN) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

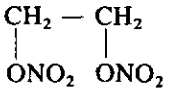
SUBSTANCE IDENTIFICATION

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate.

- **Formula:** (1) $C_3H_5N_3O_9$ (2) $C_2H_4N_2O_6$
- **Structure:**

(1) 

$\underset{ONO_2}{CH_2} - \underset{ONO_2}{CH} - \underset{ONO_2}{CH_2}$

(2) 

$\underset{ONO_2}{CH_2} - \underset{ONO_2}{CH_2}$

- **Synonyms:** (1) Anginine, blasting gelatin, blasting oil, glonoin, glycerol trinitrate, glyceryl nitrate, glyceryl trinitrate, GTN, myocon, NG, niglycon, niong, nitric acid triester of glycerol, nitrine-TDC, nitroglycerol, nitroglyn, nitrol; (2) Dinitroglycol, EGDN, ethanediol dinitrate, ethylene dinitrate, ethylene nitrate, glycol dinitrate, nitroglycol
- **Identifiers:** (1) CAS 55-63-0; RTECS QX2100000; DOT not assigned; (2) CAS 628-96-6; RTECS KW5600000; DOT not assigned
- **Appearance and odor:** (1) Pale yellow, slightly sweet smelling oil; (2) yellowish liquid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate. If not specified, data apply to both compounds.

- **Physical data**

1. Molecular weight: (1) 227.11; (2) 152.08
2. Boiling point (at 760 mmHg): (1) 256 °C (493 °F); (2) 197-200 °C (387-392 °F)
3. Explosive point: (1) 270 °C (518 °F); (2) 114 °C (237 °F)
4. Specific gravity (water = 1): (1) 1.6; (2) 1.49
5. Vapor density: (1) 7.8 (air = 1 at boiling point of NG); (2) 5.24 (air = 1 at boiling point of EGDN)
6. Melting point: (1) 13.1 °C (55.1 °F); (2) -22.3 °C (-9 °F)
7. Vapor pressure at 20 °C (68 °F): (1) 0.00012-0.011 mmHg; (2) 0.04 mmHg
8. (1) Slightly soluble in water; (2) insoluble in water

- **Reactivity**

1. Incompatibilities: Contact with acids, heat, or mechanical shock may result in explosion.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in an explosion involving NG or EGDN.

- **Flammability**

1. Flash point: Explodes
2. Autoignition temperature: (1) 270.4 °C (518 °F); (2) 195 °C (383 °F)
3. Class A Explosive (29 CFR 1910.109), Flammability Rating 2 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, NG and EGDN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for NG and EGDN is 0.2 parts of NG or EGDN per million parts of air (ppm) [2 milligrams of NG or 1 milligram of EGDN per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for NG or EGDN alone or for mixtures of the two substances is 0.1 mg/m³ as a ceiling concentration determined in any 20-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for NG or EGDN is

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

0.05 ppm (0.5 mg/m³ NG or 0.3 mg/m³ EGDN) as a time-weighted average concentration (TWA) for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational exposure limits for nitroglycerin and ethylene glycol dinitrate

	Exposure limits	
	ppm	mg/m³
OSHA PEL		
NG ceiling (Skin)*	0.2	2
EGDN ceiling (Skin)†	0.2	1
NIOSH REL		
Ceiling (20 min)	—	0.1
ACGIH TLV®		
NG TWA (Skin)	0.05	0.5
EGDN TWA (Skin)	0.05	0.3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† If the atmospheric concentration of EGDN exceeds 0.02 ppm, personal protection may be necessary to avoid headache.

HEALTH HAZARD INFORMATION

• Routes of exposure
NG and EGDN may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology
1. *Effects on animals:* Subchronic inhalation of EGDN by mice caused lethargy, skin damage, muscle spasms, and death due to circulatory and respiratory paralysis. In cats, subchronic or chronic inhalation or dermal administration of EGDN caused severe anemia, decreased appetite, seizures, hemorrhage of internal organs, and death. Chronic oral administration of NG to rats produced cancer of the liver. NIOSH will continue to monitor the research regarding NG to determine whether the collective evidence justifies controlling this chemical as a carcinogen.
2. *Effects on humans:* Acute inhalation or dermal exposure of workers to NG and EGDN has caused decreased systolic, diastolic, and pulse blood pressures due to vascular dilation. Chronic exposure to NG and EGDN has caused damage to the heart and reduced tolerance to alcohol. Chronic exposure to NG and EGDN, or to NG alone, followed by a brief or extended period away from exposure, has been associated with an increased incidence of sudden death.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to NG and EGDN can cause severe headache, dizziness, nausea, and heart palpitations.
2. *Long-term (chronic):* Exposure to NG and EGDN can cause severe chest pain (angina pectoris), which frequently occurs during brief periods away from work. Skin sensitization can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to NG or EGDN, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and nervous, cardiovascular, and hematopoietic (blood-cell-forming) systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to NG or EGDN at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical or other findings suggestive of cardiovascular disease, especially coronary artery disease. The physician should obtain baseline values for electrocardiographic studies appropriate for the age and medical history of the worker.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to NG or EGDN. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and nervous, hematopoietic, and cardiovascular sys-

tems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to NG or EGDN may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include methemoglobinemia.
2. Delayed-onset SHE's include methemoglobinemia and chest pain (angina pectoris).

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of NG and EGDN. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 20-minute sample or a series of consecutive samples that total 20 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting NG and EGDN vapors with tenax solid sorbent tubes followed by desorption with ethanol and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure NG and EGDN may also be used if available. A detailed sampling and analytical method for NG and EGDN may be found in the *NIOSH Manual of Analytical Methods* (method number 2507).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with NG and EGDN.

Workers should be provided with and required to use splash-proof safety goggles where NG or EGDN may come in contact with the eyes.

SANITATION

Clothing which is contaminated with NG or EGDN should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of NG and EGDN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of NG and EGDN's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with NG or EGDN should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle NG or EGDN should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to NG and EGDN may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for nitroglycerin and ethylene glycol dinitrate

Operations	Controls
During formulation and filling operations in the manufacture of industrial explosives and propellants	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the synthesis and handling of NG or EGDN; during the handling of industrial explosives	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the preparation and handling of dosage forms including tablets and solutions in the manufacture of pharmaceuticals	Process enclosure, local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to NG or EGDN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If NG or EGDN gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with these compounds.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to NG or EGDN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If NG or EGDN gets on the skin, wash it immediately with soap and water. If NG or EGDN penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If NG or EGDN is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing NG or EGDN, absorb on sponges or paper towels kept in a sodium carbonate solution. Remove paper towels to a secure outdoor location for burning.
4. Large quantities of liquids containing NG or EGDN may be washed with water into holding tanks where NG and EGDN can be separated. NG and EGDN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, NG and EGDN may be collected using nonsparking tools and removed to a secure, outdoor location for burning.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for nitroglycerin and ethylene glycol dinitrate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.2 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 0.5 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 2 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 20 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 40 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 40 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.1 mg/m^3 (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENEIMINE

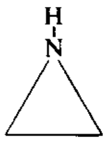
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethyleneimine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_5N
- **Structure:**



- **Synonyms:** Aminoethylene, azirane, dihydroazirene, dihydro-1h-azirine, dimethyleneimine, dimethylenimine
- **Identifiers:** CAS 151-56-4; RTECS KX5075000; DOT 1185, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Colorless volatile liquid with an intense odor like ammonia

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 43.08
2. Boiling point (at 760 mmHg): 56°C (132°F)
3. Specific gravity (water = 1): 0.8321
4. Vapor density (air = 1 at boiling point of ethyleneimine): 1.5
5. Melting point: -59°C (-74°F)
6. Vapor pressure at 20°C (68°F): 160 mmHg
7. Soluble in water

- **Reactivity**

1. Incompatibilities: Contact with silver, aluminum, or acid may cause explosive polymerization.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving ethyleneimine.

- **Flammability**

1. Flash point: -11.1°C (12°F) (closed cup)
2. Autoignition temperature: 320°C (608°F)
3. Flammable limits in air, % by volume: Lower, 3.6; Upper, 46
4. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 2 ppm
2. Eye irritation levels: 100 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ethyleneimine is 0.5 ppm [1.0 milligram of ethyleneimine per cubic meter of air (mg/m^3)] (Skin) as a time-weighted average (TWA) concentration over an 8-hour workshift. The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The OSHA standard requires implementation of stringent controls wherever ethyleneimine or solid or liquid mixtures containing at least 0.1% by weight or volume of ethyleneimine are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1012, Ethyleneimine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1.0 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyleneimine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

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- **Summary of toxicology**

1. *Effects on animals:* In rabbits and cats, acute instillation of ethyleneimine in the eyes caused damage, blindness, and death; oral administration of ethyleneimine to rats caused decreased white blood cell counts and tissue degeneration of the liver, kidneys, and heart. Subchronic subcutaneous injection of ethyleneimine in rats produced injection-site skin cancer. Chronic oral administration of ethyleneimine to mice produced cancers of the liver and lungs.
2. *Effects on humans:* Acute inhalation or dermal exposure of laboratory workers has caused central nervous system (CNS) effects, excess fluid in the lungs, damage to the liver and kidneys, and in some cases, death.

- **Signs and symptoms of exposure**

Short-term exposure (acute): Exposure to ethyleneimine can cause delayed onset headache, dizziness, nausea, and vomiting. Skin sensitization and severe irritation and inflammation of the eyes, nose, and throat can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to ethyleneimine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to ethyleneimine at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic diseases of the liver or skin or concurrent dermatitis. The physician should obtain baseline values for tests of liver function.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to ethyleneimine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: Standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to ethyleneimine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting ethyleneimine vapors with bubblers containing Folin's reagent followed by extraction with chloroform and analysis by high-pressure liquid chromatography. Direct-reading devices calibrated to measure ethyleneimine may also be used if available. A detailed sampling and analytical method for ethyleneimine may be found in the *NIOSH Manual of Analytical Methods* (method number 300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where ethyleneimine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where ethyleneimine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with ethyleneimine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of ethyleneimine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethyleneimine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove ethyleneimine from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1012:

Areas where ethyleneimine is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers are permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of ethyleneimine, local and systemic toxicity, the specific nature of the operations which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving ethyleneimine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of ethyleneimine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where ethyleneimine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of ethyleneimine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove ethyleneimine from materials, equipment, and the decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethyleneimine may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for ethyleneimine

Operations	Controls
During use in the manufacture of paper, textiles, adhesives, binders, petroleum refining products, rocket and jet fuels, lubricants, chemo-sterilant chemicals, chemotherapeutic agents, coating resins, varnishes, lacquers, agricultural chemicals, cosmetics, ion-exchange resins, photographic chemicals, colloid flocculants, and surfactants	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with ethyleneimine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to ethyleneimine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethyleneimine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to ethyleneimine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethyleneimine gets on the skin, wash it immediately with soap and water. If ethyleneimine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If ethyleneimine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing ethyleneimine, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing ethyleneimine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing ethyleneimine may be collected by vacuuming with an appropriate system. If a vacuum system is used to remove ethyleneimine, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for ethyleneimine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE OXIDE

POTENTIAL HUMAN CARCINOGEN

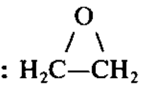
INTRODUCTION

This guideline summarizes pertinent information about ethylene oxide for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_4O

- **Structure:**



- **Synonyms:** Anprolene; dihydrooxirene; dimethylene oxide; EO; 1,2-epoxyethane; EtO; oxacyclopropane; oxane; oxiran; oxirane

- **Identifiers:** CAS 75-21-8; RTECS KX2450000; DOT 1040, label required: "Flammable Liquid"

- **Appearance and odor:** Colorless liquid or gas with an etherlike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44.06
2. Boiling point (at 760 mmHg): 10.7°C (51.3°F)
3. Specific gravity (water = 1): 0.8711
4. Vapor density (air = 1 at boiling point of ethylene oxide): 1.5
5. Melting point: -111.3°C (-168°F)
6. Vapor pressure at 20°C (68°F): 1,095 mmHg
7. Soluble in water
8. Ionization potential: 10.56 eV

- **Reactivity**

1. Incompatibilities: Ethylene oxide reacts readily with alkali metal hydroxides or highly active catalysts (e.g., anhydrous chlorides of iron, tin, or aluminum and oxides of iron or aluminum); ethylene oxide should not come in contact with copper.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving ethylene oxide.
3. Caution: Protect container against physical damage. Store in an outside area in insulated tanks or containers shielded from sun and heat. Ethylene oxide may interact with some plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -6°C (20°F) (open cup)
2. Autoignition temperature: 429°C (804°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 100
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or water spray or fog
5. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)
6. All ignition sources, including static electricity, should be controlled. Flashback along a vapor trail may occur.

- **Warning properties**

1. Odor threshold: 430 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ethylene oxide is 1 part of ethylene oxide per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that ethylene oxide be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 5 ppm [9 milligrams per cubic meter (9 mg/m^3)] as a ceiling concentration determined in any 10-minute sampling period and not to be achieved for more than 10 minutes dur-

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ing any workday. In addition, NIOSH recommends that exposure to ethylene oxide be less than 0.1 ppm (0.18 mg/m^3) as a TWA for up to an 8-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated ethylene oxide as an A2 substance (suspected of carcinogenic potential for man) having an assigned threshold limit value (TLV®) of 1 ppm (2 mg/m^3) as a TWA for a normal 8-hour workday and 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethylene oxide

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	1	—
NIOSH REL TWA		
(Ca)*	<0.1	<0.18
Ceiling (10 min/day)	5	9
ACGIH TLV® TWA		
(A2)†	1	2

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected of carcinogenic potential for man.

HEALTH HAZARD INFORMATION

• Routes of exposure

Ethylene oxide may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of ethylene oxide by rats and guinea pigs caused pulmonary edema, paralysis, and corneal opacities. Subchronic inhalation of ethylene oxide by male and female rats prior to mating and during pregnancy caused a decrease in the number of pregnant females and in the number of offspring per litter. Chronic oral administration of ethylene oxide to rats produced cancer of the forestomach; chronic inhalation produced brain tumors, leukemia, and cancer of the peritoneum.
2. *Effects on humans:* Chronic exposure to ethylene oxide has caused anemia, peripheral neuropathy, and chromosomal damage in white blood cells (lymphocytes). Exposure to ethylene oxide has been associated with increased incidences of miscarriage, leukemia, and stomach cancer.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to ethylene oxide can cause nausea, headache, weakness, vomiting, drowsiness, incoordination, and irritation of the eyes, nose, throat, and lungs. Skin contact with ethylene oxide can cause blisters, edema, burns, frostbite, and severe dermatitis.
2. *Long-term (chronic):* Exposure to ethylene oxide can cause skin sensitization, numbing of the sense of smell, and respiratory infection.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to ethylene oxide, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, gastrointestinal tract, and hematopoietic (blood cell forming), nervous, reproductive, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to ethylene oxide at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis. In addition to the medical interview and physical examination, the physician should consider obtaining additional baseline electrophysiologic and electromyographic studies and an assessment of fertility, using standardized methods and evaluation criteria.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinatons may be necessary should a worker develop symptoms that may be attributed to exposure to ethylene oxide. The interviews, examinations, and appropriate medical screening and/or biologic monitoring test should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, gastrointestinal tract, and hematopoietic, nervous, reproductive, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to ethylene oxide may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to ethylene oxide should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of ethylene oxide. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 10-minute sample or a series of consecutive samples that total 10 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting ethylene oxide vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure ethylene oxide may be used if available. A detailed sampling and analytical method for ethylene oxide may be found in the *NIOSH Manual of Analytical Methods* (method number 1607).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with liquid ethylene oxide.

SANITATION

Clothing which is contaminated with liquid ethylene oxide should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of ethylene oxide from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethylene oxide's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with ethylene oxide should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle ethylene oxide should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethylene oxide may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for ethylene oxide

Operations	Controls
During synthesis and handling of ethylene oxide	Process enclosure, local exhaust ventilation, personal protective equipment
During synthesis of ethylene glycols, glycol ethers, ethanolamines, amines, nonionic surface-active agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a sterilizing agent	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to ethylene oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethylene oxide gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to liquid ethylene oxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethylene oxide gets on the skin, wash it immediately with soap and water. If liquid ethylene oxide penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If ethylene oxide is spilled or leaked, the following steps should be taken:

1. If ethylene oxide is in the gaseous form, stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing ethylene oxide, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood duct work is free from ethylene oxide vapors. Burn the paper in a suitable location away from combustible materials.
5. Large quantities of liquids containing ethylene oxide may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Ethylene oxide should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing ethylene oxide may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134.

A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for ethylene oxide

Condition	Minimum respiratory protection*†
Concentration:	
Less than 5 ppm	Any air-purifying, full-facepiece canister respirator that provides protection against ethylene oxide and is equipped with an effective end-of-service-life indicator (ESLI)
	Any self-contained breathing apparatus equipped with a full facepiece
	Any supplied-air respirator with a full facepiece
Equal to or greater than 5 ppm, or planned or emergency entry into environments containing unknown concentrations	Any self-contained breathing apparatus equipped with a full facepiece and operated in a pressure-demand or positive-pressure mode
	Any supplied-air respirator equipped with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus equipped with a full facepiece and operated in a pressure-demand or other positive-pressure mode
Escape only	Any air-purifying, full-facepiece canister respirator that provides protection against ethylene oxide and is equipped with an effective ESLI
	Any appropriate escape-type, self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of <0.1 ppm (<0.18 mg/m^3) (TWA).

Occupational Health Guideline for Ethyl Ether

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5OC_2H_5$
- Synonyms: Diethyl ether; ethyl oxide; ether; diethyl oxide; sulfuric ether
- Appearance and odor: Colorless liquid with a characteristic, sweet ether odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl ether is 400 parts of ethyl ether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1200 milligrams of ethyl ether per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl ether can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl ether may cause irritation of the eyes, nose, and throat. It may also cause dizziness, drowsiness, unconsciousness, and death.

2. Long-term Exposure: Prolonged overexposure may cause loss of appetite, dizziness, drowsiness, headache, exhaustion, excitation, and mental disturbances. It may also increase the severity of the effects of drinking alcoholic beverages. Repeated exposure may be habit forming.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl ether at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl ether exposure.

—Skin disease: Ethyl ether can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethyl ether is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although ethyl ether is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl ether might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl ether has predominantly narcotic properties leading to anesthesia; it is also an eye and respiratory irritant. Continued inhalation of 2000 ppm in human subjects may produce dizziness. Higher concentrations produce vomiting, pallor, and irregular respiration. Temporary aftereffects are salivation, vomiting, respi-

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ratory tract irritation, headache, and either depression or excitation. Chronic exposure results in some persons in anorexia, exhaustion, headache, drowsiness, dizziness, excitation, and psychic disturbances. Albuminuria has been reported. Tolerance may be acquired through repeated exposures. Ethyl ether is a mild skin irritant; repeated exposure causes drying and cracking. The vapor is irritating to the eye, and the undiluted liquid causes painful inflammation of a transitory nature. Human subjects found 200 ppm irritating to the nose, but not to the eyes or throat. Permanent aftereffects are rare.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): 35 C (95 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of ethyl ether): 2.6
5. Melting point: −123 C (−190 F)
6. Vapor pressure at 20 C (68 F): 442 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 7.5
8. Evaporation rate (butyl acetate = 1): 37.5

- **Reactivity**

1. Conditions contributing to instability: Heat; sunlight
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl ether.
4. Special precautions: Ethyl ether will attack some forms of plastics, rubber, and coatings. Ethers, which have been in contact with air or exposed to light for a long time, may contain peroxides. Ethers which contain peroxides may explode when the caps or stoppers of their containers are removed. Ethyl ether, being a nonconductor, may accumulate static electric charges that may result in ignition of its vapors.

- **Flammability**

1. Flash point: −45 C (−49 F) (closed cup)
2. Autoignition temperature: 160 C (320 F)
3. Flammable limits in air, % by volume: Lower: 1.9; Upper: 36.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for ethyl ether of 0.33 ppm. Patty notes that the odor is pungent.
2. Eye Irritation Level: Grant states that ethyl ether "causes a transitory smarting sensation if splashed in the eye or if a high vapor concentration contacts the eye, but momentary exposure generally does not cause injury. Prolonged exposure of the cornea to high concentration of ether vapor, such as employed in general anesthesia, does cause superficial epithelial injury, from which recovery is usually prompt." Patty also reports that in high concentrations ethyl ether causes eye irritation.
3. Other Information: Patty reports that "Nelson et al. reported that human subjects found ethyl ether irritating to the nose, but not to the eyes or throat, at a vapor concentration of 200 ppm."
4. Evaluation of Warning Properties: Through its odor and nasal irritation, ethyl ether can be detected below the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl ether vapors using an adsorption tube with subsequent desorption with ethyl acetate and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl ether may be used. An analytical method for ethyl ether is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl ether.
- Clothing wet with liquid ethyl ether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl ether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl ether, the person performing the operation should be informed of ethyl ether's hazardous properties.
- Any clothing which becomes wet with liquid ethyl ether should be removed immediately and not reworn until the ethyl ether is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl ether may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in manufacture of smokeless powder	Local exhaust ventilation; general dilution ventilation
Use as a laboratory solvent and chemical extractant	General dilution ventilation; personal protective equipment
Use as a solvent cleaning agent in shoe and textile industries	General dilution ventilation; personal protective equipment
Use as an anesthetic	General dilution ventilation
Liberation from manufacture of alkali or sodium ethylxanthotes by heated processes; from manufacture of warm-process pharmaceuticals; from manufacture of chemicals from cold processes— Grignard reactions and acetic acid recovery	Process enclosure; general dilution ventilation; local exhaust ventilation
Use as a solvent in manufacture of textiles, cellulose acetate, plastics, and dyes	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during manufacture of cold-process pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an additive in motor fuels, perfumes, and denatured alcohol	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in the priming of gasoline engines in cold climates	General dilution ventilation
Liberation during refueling of diesel engines in cold climates	General dilution ventilation
Use as an anesthetic by animal handlers	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl ether gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl ether gets on the skin, promptly wash the contaminated skin with water if the ethyl ether has not already evaporated. If ethyl ether soaks through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl ether, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl ether has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Ethyl ether should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Ethyl ether may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol, and by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ETHYL ETHER

Condition	Minimum Respiratory Protection* Required Above 400 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
4000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
19,000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 19,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Formate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HCOOC_2H_5$
- Synonyms: Ethyl methanoate; formic acid ethyl ester
- Appearance and odor: Colorless liquid with a fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl formate is 100 parts of ethyl formate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of ethyl formate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl formate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl formate may cause irritation of the eyes, nose, throat. and skin. At high concentrations it may cause drowsiness and unconsciousness.

2. Long-term Exposure: Long-term overexposure to ethyl formate may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl formate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl formate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl formate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl formate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: This substance is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethyl formate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although ethyl formate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl formate is irritating to the eyes and nose at concentrations of 330 ppm. Narcosis occurs in animals, but only at exposure levels near the lethal concentration of 10,000 ppm. Dogs exposed to this very high concentration died of pulmonary edema. Rats survived at 4000 ppm. Application to the skin caused only slight irritation; when dropped into the eye, it caused moderate injury to the cornea. No chronic systemic effects have been reported in humans.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74
2. Boiling point (760 mm Hg): 54.5 C (130 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of ethyl formate): 2.6
5. Melting point: −79 C (−110 F)
6. Vapor pressure at 20 C (68 F): 194 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 13.6
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl formate.
4. Special precautions: None

- **Flammability**

1. Flash point: −20 C (−4 F) (closed cup)
2. Autoignition temperature: 455 C (851 F)
3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 16
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No information is available concerning the odor threshold of ethyl formate.
2. Eye Irritation Level: According to the *Documentation of TLV's*, "in man, a concentration of 330 ppm produced a slight irritation of the eyes and a rapidly increasing nasal irritation . . . . A threshold limit of 100 ppm is recommended to prevent eye and nasal irritation."
3. Evaluation of Warning Properties: Since eye and nasal irritation occur at a concentration which is approximately only three times the permissible exposure limit, ethyl formate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ethyl formate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl formate may be used. An analytical method for ethyl formate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl formate.
- Any clothing which becomes wet with liquid ethyl formate should be removed immediately and not reworn until the ethyl formate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl formate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid ethyl formate should be promptly washed or showered to remove any ethyl formate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl formate may occur and control methods which may be effective in each case:

Operation	Controls
Use during spray, brush, or dip applications of lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for cellulose acetate in artificial silk manufacture	General dilution ventilation; personal protective equipment
Use in shoe industry to dissolve celluloid heel coverings; use as a solvent in manufacture of artificial leather	General dilution ventilation; personal protective equipment
Use in manufacture of safety glass	General dilution ventilation
Use as a fumigant and larvacide for tobacco, cereals, and dried fruits	Personal protective equipment
Liberation during use as an intermediate in organic synthesis	General dilution ventilation
Liberation during formulation of synthetic flavors	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ethyl formate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ethyl formate gets on the skin, immediately flush the contaminated skin with water. If ethyl formate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl formate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ethyl formate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl formate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Ethyl formate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Ethyl formate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

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- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
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RESPIRATORY PROTECTION FOR ETHYL FORMATE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLIDENE NORBORNENE

INTRODUCTION

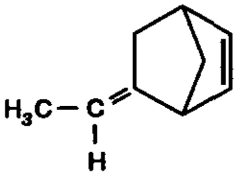
This guideline summarizes pertinent information about ethylidene norbornene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_9H_{12}

- **Structure**



- **Synonyms**

5-Ethylidene-2-norbornene; 5-ethylidenebicyclo(2,2,1)hept-2-ene; ENB

- **Identifiers**

1. CAS No.: 16219-75-3
2. RTECS No.: RB9450000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Ethylidene norbornene is a combustible, colorless to white liquid with a turpentine-like odor. An odor threshold for ethylidene norbornene has been reported in the range of 0.007 to 0.014 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 120.2
2. Boiling point (760 mm Hg): 147.6°C (298°F)
3. Specific gravity (water = 1): 0.896 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of ethylidene norbornene): 4.1
5. Freezing/Melting point: -80°C (-112°F)
6. Vapor pressure at 20°C (68°F): 4.2 mm Hg
7. Solubility: Data not available
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, open flame, and oxygen.

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2. Incompatibilities: Contact of ethylidene norbornene with oxygen can cause violent reactions.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide) may be released in a fire involving ethylidene norbornene.

4. Special precautions: Because of its reactivity, ethylidene norbornene must be stabilized with tert-butyl catechol.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for ethylidene norbornene; however, other sources report that this substance is combustible.

1. Flash point: 38.33°C (101°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving ethylidene norbornene. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving ethylidene norbornene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethylidene norbornene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethylidene norbornene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (25 mg/m^3) as a ceiling limit for ethylidene norbornene. The ceiling limit should not be exceeded during any part of the workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ethylidene norbornene a ceiling limit value of 5 ppm (25 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation associated with ethylidene norbornene exposure and renal, urogenital, and bone marrow effects found in animals exposed to ethylidene norbornene [NIOSH 1992]. The ACGIH limit is based on the risk of eye and nose irritation associated with exposure to ethylidene norbornene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ethylidene norbornene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Ethylidene norbornene causes irritation of the eyes and skin, as well as liver and testicular toxicity in animals. In contact with the skin of rabbits, ethylidene norbornene caused a mild degree of skin irritation [NIOSH 1994]. The dermal LD_{50} in rabbits is 8,189 mg/kg [NIOSH 1994]. In contact with the eyes of rabbits, this substance produced transient conjunctival irritation [Grant 1986]. The 4-hr LC_{50} is 1,246 ppm in rats and 732 ppm in mice [NIOSH 1994]. The oral LD_{50} is 2,527 mg/kg in rats and 3,250 mg/kg in mice. Dogs exposed to a 93-ppm concentration of ethylidene norbornene for 7 hours/day, 5 days/week, for a total of 89 exposures showed slight blood changes and, at autopsy, hepatic lesions and testicular atrophy [Hathaway et al. 1991]. When dogs were exposed to a concentration of 61 ppm on the same regimen, less severe lesions of these organs were seen at post mortem. At an ethylidene norbornene concentration of 22 ppm, no damage was noted [Hathaway et al. 1991]. Twenty-one of twenty-four rats inhaling a 237-ppm concentration of ethylidene norbornene on the same schedule died. Liver

lesions, atrophy of the testicles, and hydrothorax were observed. No deaths occurred from 90 ppm, but liver lesions were evident [ACGIH 1991].

2. *Effects on Humans:* Ethylidene norbornene causes eye, nose, and upper respiratory tract irritation in humans. Volunteers exposed for 30 minutes to a 6-ppm concentration of ethylidene norbornene reported transient eye irritation, and, at a concentration of 11 ppm, both eye and nose irritation were experienced [ACGIH 1991]. In contact with the skin, ethylidene norbornene caused reddening and defatting [USCG 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to ethylidene norbornene include redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, and redness and inflammation of the skin.

2. *Chronic exposure:* Repeated exposure to ethylidene norbornene may damage the liver, kidneys, and lungs in humans.

- **Emergency procedures:**

> WARNING!
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposures to concentrated solutions, vapors, mists, or aerosols of ethylidene norbornene. ***Immediately and thoroughly*** flush eyes with large amounts of water occasionally lifting the lower and upper eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if ethylidene norbornene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ethylidene norbornene and may lead to worker exposures to this substance:

—Manufacture of pharmaceuticals and pesticides

—Preparation of specialty resins

—Use as the third monomer in ethylene-propylene diene monomer elastomers

The following methods are effective in controlling worker exposures to ethylidene norbornene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to ethylidene norbornene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, upper respiratory tract, reproductive system, skin, liver, and kidneys. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ethylidene norbornene at or below the prescribed exposure limit. A licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, respiratory tract, skin, liver, or kidneys or disturbances in reproductive function.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ethylidene norbornene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethylidene norbornene on the eyes, respiratory tract, skin, liver, kidneys, or reproductive function. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ethylidene norbornene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

No sampling and analytical method is available to determine a worker's exposure to airborne ethylidene norbornene.

PERSONAL HYGIENE

If ethylidene norbornene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with ethylidene norbornene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of ethylidene norbornene, particularly its potential to be irritating to the skin.

A worker who handles ethylidene norbornene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where ethylidene norbornene or a solution containing ethylidene norbornene is handled, processed, or stored.

STORAGE

Ethylidene norbornene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Ethylidene norbornene must be stored under an inert (oxygen free) atmosphere (i.e., a nitrogen atmosphere) or be stabilized with tert-butyl catechol. Containers of ethylidene norbornene should be protected from physical damage and should be stored away from oxygen, heat, sparks, and open flame. Because containers that formerly contained ethylidene norbornene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethylidene norbornene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors.
6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the ethylidene norbornene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Ethylidene norbornene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental

Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of ethylidene norbornene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of ethylidene norbornene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although ethylidene norbornene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ethylidene norbornene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with ethylidene norbornene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to ethylidene norbornene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to ethylidene norbornene.

Safety glasses, goggles, or face shields should be worn during operations in which ethylidene norbornene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ethylidene norbornene. Contact lenses should not be worn if the potential exists for ethylidene norbornene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about ethyl mercaptan for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_5SH
- **Structure:** $CH_3—CH_2—SH$
- **Synonyms:** Ethanethiol, ethyl sulfhydrate, ethyl thiolalcohol, thioethanol, thioethyl alcohol
- **Identifiers:** CAS 75-08-1; RTECS DI9625000; DOT 2363, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a penetrating odor like garlic or decayed cabbage

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 62.13
2. Boiling point (at 760 mmHg): 35°C (95°F)
3. Specific gravity (water = 1): 0.839
4. Vapor density (air = 1 at boiling point of ethyl mercaptan): 2.1
5. Melting point: -148°C (-234°F)
6. Vapor pressure at 20°C (68°F): 442 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.5
8. Evaporation rate (butyl acetate = 1): 24.9
9. Saturation concentration in air (approximate) at 20°C (68°F): 58.2% (582,000 ppm)
10. Ionization potential: 9.28 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving ethyl mercaptan.
3. Caution: Ethyl mercaptan will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: <−18°C (<0°F) (closed cup)
2. Autoignition temperature: 300°C (572°F)
3. Flammable limits in air, % by volume: Lower, 2.8; upper, 18
4. Extinguishant: Carbon dioxide or dry chemicals for small fires, alcohol foam for large fires
5. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 0.26 to 0.97 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, ethyl mercaptan can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ethyl mercaptan is 10 parts of ethyl mercaptan per million parts of air (ppm) [25 milligrams of ethyl mercaptan per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.5 ppm (1.3 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1 mg/m^3) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethyl mercaptan

	Exposure limits	
	ppm	mg/m^3
OSHA PEL ceiling	10	25
NIOSH REL ceiling (15 min)	0.5	1.3
ACGIH TLV® TWA	0.5	1

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HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl mercaptan may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of ethyl mercaptan by rats and mice caused irritation of mucous membranes, incoordination, staggering gait, weakness, partial skeletal muscle paralysis, deficient oxygenation of the blood (cyanosis), respiratory depression, coma, and death. Sublethal doses produced swelling, fatty degeneration, and tissue destruction (necrosis) of the liver and cloudy swelling in the kidneys. Undiluted ethyl mercaptan instilled in the eyes of rabbits caused slight-to-moderate irritation. Chronic inhalation of ethyl mercaptan by rats and rabbits caused cardiovascular disorders, decreased gas exchange, increased nervous excitability, and effects on the blood-forming system including decreased red blood cell counts.
2. *Effects on humans:* Persons clinically exposed to low concentrations of ethyl mercaptan over a 5- to 10-day period reported an altered taste reaction to bitter and sweet substances and a rise in olfactory threshold.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to ethyl mercaptan can cause headache, nausea, weakness, fatigue, incoordination, and irritation of the mucous membranes.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to ethyl mercaptan, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, and nervous and respiratory systems.

Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to ethyl mercaptan at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin and respiratory system.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to ethyl mercaptan. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of ethyl mercaptan. Each measurement to determine the

NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Currently there is no NIOSH-validated method for sampling and analysis of ethyl mercaptan. Detector tubes or other direct-reading devices calibrated to measure ethyl mercaptan may be used if available.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with ethyl mercaptan.

Workers should be provided with and required to use splash-proof safety goggles where ethyl mercaptan may come in contact with the eyes.

SANITATION

Clothing which is contaminated with ethyl mercaptan should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethyl mercaptan's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with ethyl mercaptan should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle ethyl mercaptan should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethyl mercaptan may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for ethyl mercaptan

Operations	Controls
During use as a fuel gas odorant	Process enclosure, general dilution ventilation, personal protective equipment
During use as a chemical intermediate or raw material in the production of insecticides, anti-oxidants, plastics, and pharmaceuticals	Process enclosure, general dilution ventilation, personal protective equipment
During use as a stabilizer (0.5 to 5% quantities for stabilizing synthetic resins, rubber, polyvinyl compounds, and adhesives)	Process enclosure, general dilution ventilation, personal protective equipment
During synthesis and processing of ethyl mercaptan	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent for elastomeric polymers and oil soluble dyes in industrial stains and quicksetting rubber cements	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During cleaning and maintenance of storage vessels and equipment	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to ethyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethyl mercaptan gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to ethyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethyl mercaptan gets on the skin, wash it immediately with soap and water. If ethyl mercaptan penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If ethyl mercaptan is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing ethyl mercaptan, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from ethyl mercaptan vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing ethyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material, treated with hypochlorite, and placed in an appropriate container. Ethyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing ethyl mercaptan may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for ethyl mercaptan

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator Any self-contained breathing apparatus Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 12.5 ppm	Any supplied-air respirator operated in a continuous flow mode Any powered air-purifying respirator with organic vapor cartridge(s)
Less than or equal to 25 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 500 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Less than or equal to 1,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 1,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 ppm (1.3 mg/m^3) (ceiling).

Occupational Health Guideline for n-Ethylmorpholine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_{13}ON$
- Synonyms: 4-Ethylmorpholine
- Appearance and odor: Colorless liquid with an ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for N-ethylmorpholine is 20 parts of N-ethylmorpholine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 94 milligrams of N-ethylmorpholine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Ethylmorpholine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: n-Ethylmorpholine may cause irritation of the eyes, nose, and throat. Eye exposure may result in foggy vision and seeing halos around lights.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to N-ethylmorpholine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to n-ethylmorpholine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from n-ethylmorpholine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of N-ethylmorpholine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: n-Ethylmorpholine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Liver disease: Although N-ethylmorpholine is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although N-ethylmorpholine is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

n-Ethylmorpholine vapor causes visual disturbances and irritates mucous membranes. Some rats died after exposure to 2000 ppm for 4 hours. In an experimental study, humans exposed to 100 ppm for 2-½ minutes experienced irritation of eyes, nose, and throat, while 50 ppm produced lesser irritation. Workers exposed to low vapor concentrations for several hours reported temporarily fogged vision with rings around lights; corneal edema was observed; this effect is thought to occur

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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when air concentrations of substituted morpholines are 40 ppm or higher; the symptoms usually appear at the end of the work day and clear within 3 to 4 hours after cessation of exposure. The liquid when placed into the eye of a rabbit caused corneal haziness, sloughing, and irregularities of the surface, characteristic of severe desiccation. On the skin of a rabbit, the undiluted liquid produced no reaction, unlike unsubstituted morpholine, which is a severe skin irritant.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 115.2
2. Boiling point (760 mm Hg): 138.6 C (281 F)
3. Specific gravity (water = 1): 0.91
4. Vapor density (air = 1 at boiling point of N-ethylmorpholine): 4.0
5. Melting point: −63 C (−81 F)
6. Vapor pressure at 20 C (68 F): 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 0.8

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid N-ethylmorpholine with strong acids will cause violent spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia, oxides of nitrogen, and carbon monoxide) may be released in a fire involving N-ethylmorpholine.
4. Special precautions: Liquid N-ethylmorpholine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 32.2 C (90 F) (closed cup)
2. Autoignition temperature: 185 C (365 F)
3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 9.8
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, in a study with human volunteers, the ammonia odor of N-ethylmorpholine is noticeable at 25 ppm. The odor becomes stronger at higher concentrations, but olfactory fatigue occurs.
2. Eye Irritation Level: Grant reports the occurrence of "transient edema of the corneal epithelium in workers exposed to 40 ppm or more in air during the work day."

The *Documentation of TLV's* reports that eye irritation was noted in human volunteers exposed to 100 ppm N-ethylmorpholine for 2-½ minutes. "Slight if any irritation" occurred at 50 ppm.

3. Other Information: The *Documentation of TLV's* reports that nose and throat irritation also occurred among human volunteers exposed to 100 ppm N-ethylmorpholine for 2-½ minutes. "Slight if any irritation" occurred at 50 ppm.
4. Evaluation of Warning Properties: Since olfactory fatigue occurs during exposure to N-ethylmorpholine, odor is not considered to be a good warning property. In addition, since irritation does not definitely occur until a concentration several times greater than the permissible exposure limit, N-ethylmorpholine is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of N-ethylmorpholine in an adsorption tube containing silica gel, followed by desorption with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure N-ethylmorpholine may be used. An analytical method for N-ethylmorpholine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid N-ethylmorpholine.
- Clothing contaminated with N-ethylmorpholine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of N-ethylmorpholine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the N-ethylmorpholine, the person performing the operation should be informed of N-ethylmorpholine's hazardous properties.
- Where exposure of an employee's body to liquid N-ethylmorpholine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with N-ethylmorpholine should be removed promptly and not reworn until the N-ethylmorpholine is removed from the clothing.
- Any clothing which becomes wet with liquid N-ethylmorpholine should be removed immediately and not reworn until the N-ethylmorpholine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid N-ethylmorpholine or solutions containing N-ethylmorpholine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to N-ethylmorpholine or solutions containing more than 15% N-ethylmorpholine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with N-ethylmorpholine should be promptly washed or showered to remove any N-ethylmorpholine.
- Employees who handle liquid N-ethylmorpholine should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to N-ethylmorpholine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a catalyst for flexible, semi-flexible, and rigid polyurethane foam production	Local exhaust ventilation; personal protective equipment
Use in polymer technology as a promoter for resin surface curing, and as a stabilizer for fiber spinning solutions	Local exhaust ventilation; personal protective equipment
Use in manufacture of vat dyes; use in manufacture of pharmaceuticals in purification of Penicillin G	Local exhaust ventilation; personal protective equipment
Use in organic synthesis as a special solvent, pH regulator, and for preparation of chemical intermediates	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If N-ethylmorpholine or solutions containing N-ethylmorpholine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If N-ethylmorpholine gets on the skin, promptly flush the contaminated skin with water. If N-ethylmorpholine soaks through the clothing, remove the clothing immediately and flush the skin with water.

- **Breathing**

If a person breathes in large amounts of N-ethylmorpholine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When N-ethylmorpholine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Under-

stand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If N-ethylmorpholine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. n-Ethylmorpholine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

n-Ethylmorpholine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on N-ethylmorpholine, look up N-ethylmorpholine in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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RESPIRATORY PROTECTION FOR N-ETHYLMORPHOLINE

Condition	**Minimum Respiratory Protection* Required Above 20 ppm**
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ethyl Silicate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5O)_4Si$ or $(C_2H_5)_4SiO_4$
- Synonyms: Ethyl silicate, condensed; tetraethyl orthosilicate; tetraethyl silicate; ethyl orthosilicate tetraethoxysilane
- Appearance and odor: Colorless liquid with a mild, sweet, alcohol-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl silicate is 100 parts of ethyl silicate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 850 milligrams of ethyl silicate per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for ethyl silicate a Threshold Limit Value of 10 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl silicate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to ethyl silicate may irritate the eyes and nose. In animals, exposure to ethyl silicate has caused severe breathing difficulties, liver damage, kidney damage, and anemia. Repeated applications of ethyl silicate to animal skin has caused the skin to become dry.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl silicate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl silicate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl silicate exposure.

—Chronic respiratory disease: Ethyl silicate causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl silicate might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Ethyl silicate causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Ethyl silicate causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Blood disease: Ethyl silicate causes anemia in animals. Persons with pre-existing blood disorders may be more susceptible to the effects of this agent.

—Skin disease: Ethyl silicate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl silicate vapor irritates the eyes and nose and in animals causes lung, liver, and kidney damage. Exposure of guinea pigs to 2530 ppm for 4 hours was lethal to more than half of the animals; usually death was delayed and a result of pulmonary edema; effects were

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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irritation of eyes and nose, lacrimation, tremor, dyspnea, and narcosis; some surviving animals later developed a delayed profound anemia. Exposure of rats to 1000 ppm for up to three 7-hour periods was fatal; autopsy findings were marked tubular degeneration and necrosis of the kidneys, mild liver damage, and slight pulmonary edema and hemorrhage. In rats exposed to 125 ppm for 15 to 20 7-hour periods, slight to moderate kidney damage was observed, but no pathologic changes were detected in the liver or lungs. In humans, the eyes and nose are affected by brief exposures as follows: 3000 ppm, extremely irritating and intolerable; 1200 ppm, lacrimation and stinging; 700 ppm, mild stinging; 250 ppm, slight tingling; Instillation of the liquid into the rabbit eye caused immediate marked irritation which was reversible. Repeated or prolonged skin contact with the liquid may cause dermatitis due to its solvent effect.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 169 C (336 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of ethyl silicate): 7.2
5. Melting point: Less than −85 C (−121 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts slowly to form ethyl alcohol and silica gel
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause containers to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with water causes formation of volatile and flammable ethyl alcohol.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl silicate.
4. Special precautions: Ethyl silicate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 37.2 C (99 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 23
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: According to Grant, ethyl silicate can be detected by odor at 85 ppm.
2. Irritation levels: Grant states that "observations were made of the effect of various concentrations on the human experimenters: 3000 ppm was found to be extremely irritating to the eyes and nose; 1200 ppm stings eyes and nose and produces tears; 700 ppm mildly stings eyes and nose; 250 ppm makes the eyes and nose tingle slightly . . . ."
3. Evaluation of Warning Properties: Since the threshold of odor is below the permissible exposure limit, and since the thresholds of eye and nasal irritation are within three times the permissible exposure limit, ethyl silicate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube packed with XAD-2 resin, followed by desorption with carbon disulfide and gas chromatographic analysis. Detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl silicate may be used. An analytical method for ethyl silicate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl silicate.

- Clothing wet with liquid ethyl silicate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl silicate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl silicate, the person performing the operation should be informed of ethyl silicate's hazardous properties.
- Any clothing which becomes wet with liquid ethyl silicate should be removed immediately and not reworn until the ethyl silicate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid ethyl silicate contacting the eyes.

SANITATION

- Skin that becomes wet with liquid ethyl silicate should be promptly washed or showered with soap or mild detergent and water to remove any ethyl silicate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl silicate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a bonding agent for investment castings, ceramic shells, crucibles, and types of refractory shapes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a protective coating for paints, lacquers, and films	General dilution ventilation; personal protective equipment
Use in manufacture of protective and preservative coatings for protection from corrosion, chemicals, heat, scratches, and fire	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in impregnation of porous materials to increase strength, hardness, stiffness, and abrasion	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a waterproofing and weatherproofing agent in porous rock	General dilution ventilation; personal protective equipment
Use as a chemical intermediate; use as a gelling agent in organic liquids; use as a coating agent inside electric lamp bulbs, and in the synthesis of fused quartz	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in textile industry in aqueous emulsions, deluster and fireproofing, and to increase strength; use as a component of lubricants as mold release agent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid ethyl silicate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid ethyl silicate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid ethyl silicate soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ethyl silicate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid ethyl silicate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ethyl silicate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Ethyl silicate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of ethyl silicate vapors are permitted.

- Waste disposal methods:

Ethyl silicate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHYL SILICATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ferbam

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $((CH_3)_2NCS_2)_3Fe$
- Synonyms: Ferric dimethyldithiocarbamate; tris(dimethyldithiocarbamato)iron
- Appearance and odor: Odorless black solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ferbam is 15 milligrams of ferbam per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for ferbam a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ferbam can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may also affect the body if it is swallowed.

- **Effects of overexposure**

Ferbam dust may cause irritation of the eyes and respiratory tract. Swallowing large amounts of ferbam or liquids containing ferbam may cause gastrointestinal disturbances. Ferbam may also cause a skin rash in people who are allergic to sulfur.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ferbam.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ferbam at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ferbam exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ferbam might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Ferbam can cause dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ferbam dust irritates the eyes and respiratory tract. In guinea pigs given ferbam by stomach tube, the lethal range was 450 to 2000 mg/kg; the animals became stuporous and died in coma. Ten of 20 rats died from a diet containing 0.5% ferbam for 30 days; there was a slight and ill-defined tendency toward anemia; at autopsy there was no evidence of a regularly appearing tissue injury; minor abnormalities of the lung, liver, kidney and bone marrow were observed in a few animals. In humans, the dust is irritating to the eyes and respiratory tract; it causes dermatitis in individuals sensitized to sulfur. Large oral doses cause gastrointestinal disturbances. Because of chemical similarity to Antabuse, absorption of ferbam may potentiate action of ethyl alcohol.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 416.5
  2. Boiling point (760 mm Hg): Decomposes

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will *assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance* with all requirements of OSHA regulations.

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3. Specific gravity (water = 1): Greater than 1

4. Vapor density (air = 1 at boiling point of ferbam): Not applicable

5. Melting point: 180 C (356 F) (decomposes)

6. Vapor pressure at 20 C (68 F): Essentially zero

7. Solubility in water, g/100 g water at 20 C (68 F): 0.012

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 180 C (356 F) cause decomposition with formation of toxic gases.

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of sulfur and nitrogen and carbon monoxide) may be released in a fire involving ferbam.

4. Special precautions: None.

- **Flammability**

1. Flash point: Not applicable

2. Minimum ignition temperatures: 280 C (536 F) (cloud); 150 C (302 F) (layer)

3. Minimum explosive dust concentration: 0.055 g/l

4. Extinguishant: Water, dry powder

- **Warning properties**

Grant states that ferbam "is a fungicide, the dust of which is irritating to the eye, nose, throat, and skin."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for ferbam had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with ferbam or liquids containing ferbam.
- If employees' clothing may have become contaminated with ferbam or liquids containing ferbam, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with ferbam should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ferbam from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ferbam, the person performing the operation should be informed of ferbam's hazardous properties.
- Non-impervious clothing which becomes contaminated with ferbam should be removed promptly and not reworn until the ferbam is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where ferbam or liquids containing ferbam may contact the eyes.

SANITATION

- Skin that becomes contaminated with ferbam should be promptly washed or showered with soap or mild detergent and water to remove any ferbam.
- Eating and smoking should not be permitted in areas where solid ferbam is handled, processed, or stored.
- Employees who handle ferbam or liquids containing ferbam should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ferbam may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of fungicides	Process enclosure; local exhaust ventilation; personal protective equipment
Application as a foliage fungicide for control of scab and rust diseases	Personal protective equipment
Manufacture of ferbam	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ferbam or liquids containing ferbam get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ferbam or liquids containing ferbam get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If ferbam or liquids containing ferbam penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ferbam, move the exposed person to fresh air at once.

- **Swallowing**

When ferbam or liquids containing ferbam have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If ferbam is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing ferbam should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Ferbam may be disposed of in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on ferbam, look up ferbam in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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RESPIRATORY PROTECTION FOR FERBAM

Condition	Minimum Respiratory Protection* Required Above 15 mg/m^3
Particulate Concentration	
75 mg/m^3 or less**	Any dust respirator, except single-use.
150 mg/m^3 or less**	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7500 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7500 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Ferrovanadium Dust

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Ferrovanadium contains varying amounts of iron and vanadium and several other minor constituents (e.g., silicon, manganese, chromium, and nickel). Ferrovanadium has been produced with as little as 35% vanadium and as much as 85% vanadium.
- Synonyms: None
- Appearance: Dark, odorless solid particles.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ferrovanadium dust is 1 milligram of ferrovanadium dust (as vanadium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to 1 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Vanadium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ferrovanadium dust can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

Ferrovanadium dust causes irritation of the eyes, nose, and throat.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ferrovanadium dust.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ferrovanadium dust at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin and eyes should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ferrovanadium dust may cause respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ferrovanadium dust is reported to cause asthmatic-like symptoms. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Ferrovanadium dust is a mild irritant of the eyes and respiratory tract. Animals exposed for 1 hour on alternate days for 2 months to very high concentrations (1000 to 2000 mg/m^3) developed chronic bronchitis and pneumonitis. Workers exposed to unspecified concentrations developed a slight irritation of the eyes and respiratory tract. Systemic effects have not been reported from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: Not applicable
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): Greater than 1
  4. Vapor density (air = 1 at boiling point of ferrovanadium dust): Not applicable

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: 400 C (752 F) (layer); 440 C (824 F) (cloud)
3. Minimum explosive concentration: 1.3 grams per cubic meter
4. Extinguishant: Dry sand, dry dolomite, dry graphite powder

- **Warning properties**

Ferrovanadium dust may cause eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ferrovanadium dust, followed by chemical treatment and atomic absorption spectrophotometry. An analytical method for ferrovanadium dust is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

- Eating and smoking should not be permitted in areas where ferrovanadium dust is generated in handling, processing, or storing of ferrovanadium.
- Employees who handle ferrovanadium dust should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ferrovanadium dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture and processing of ferrovanadium alloy	General dilution ventilation; personal protective equipment
Use in the production of steel as an additive to produce grain refinement and hardenability	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ferrovanadium dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention . Contact lenses should not be worn when working with this chemical.

- **Breathing**

If a person breathes in large amounts of ferrovanadium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of release until cleanup has been completed.
- If potentially hazardous amounts of ferrovanadium dust are inadvertently released, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of release to disperse the dust.
3. Collect released material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Ferrovanadium dust may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR FERROVANADIUM DUST

Condition	Minimum Respiratory Protection* Required Above 1 mg/m^3
Particulate Concentration	
5 mg/m^3 or less	Any dust and mist respirator, except single-use respirator.
10 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 500 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Fluorine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: F_2
- Synonyms: None
- Appearance and odor: Pale yellow gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluorine is 0.1 part of fluorine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of fluorine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for fluorine a Threshold Limit Value of 1 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Fluorine can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to fluorine gas may cause irritation of the eyes, nose, throat, lungs, and skin. It may cause severe breathing difficulties which may be delayed in onset. At high concentrations, as when coming directly from a gas cylinder, fluorine may cause severe burns of the eyes and skin. In animal experiments, exposure to fluorine has produced kidney and liver damage.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to fluorine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to fluorine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Fluorine causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEC (1 sec): Fluorine is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Fluorine gas is a severe irritant of the eyes, mucous membranes, and skin. It reacts with water to produce ozone and hydrofluoric acid. The LC50 in mice for 60 minutes was 150 ppm; effects were irritation of the eyes and nose and the delayed onset of dyspnea and lethargy; autopsy findings included marked pulmonary congestion and hemorrhage. Mice exposed to sublethal concentrations had pulmonary irritation and delayed development of focal necrosis in the liver and kidneys. In humans the inhalation of high concentrations causes laryngeal spasm and bronchospasm, followed by the delayed onset of pulmonary edema; there may also be

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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gastrointestinal disturbances. Two human subjects found momentary exposure to 50 ppm intolerable; 25 ppm was tolerated briefly, but both subjects developed sore throat and chest pain which persisted for 6 hours. A blast of fluorine gas on the shaved skin of a rabbit caused a second-degree burn; lower concentrations cause severe burns of insidious onset resulting in ulceration, similar to those produced by hydrogen fluoride.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 38
2. Boiling point (760 mm Hg): −188 C (−307 F)
3. Specific gravity (water = 1): (Liquid) 1.5 at boiling point
4. Vapor density (air = 1 at boiling point of fluorine): 1.3
5. Melting point: −219 C (−363 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Fluorine is a dangerously reactive gas. Contact with water causes formation of toxic hydrogen fluoride gas. It reacts vigorously with most oxidizable materials at room temperature, frequently with ignition. It reacts with nitric acid to form fluorine nitrate, which is an explosive gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride) may be released when fluorine decomposes.
4. Special precautions: Fluorine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizer.
2. Compressed gas cylinders containing fluorine should be stored in accordance with 29 CFR 1910.101.

- **Warning properties**

1. Odor Threshold: The *Hygienic Information Guide* for fluorine of the Commonwealth of Pennsylvania Division of Occupational Health states that fluorine "can be detected by odor in concentrations of only a few parts per million." Deichmann and Gerarde note that the odor is "sharp, penetrating, and characteristic."
2. Eye Irritation Level: Grant states that "exposure of human volunteers to fluorine in air showed that, although it caused very little irritation up to 25 ppm, it caused much irritation of the eyes and nose at 100 ppm. However, there were no aftereffects from exposure of the eyes to 100 ppm for one-half minute. Contact with high concentrations of fluorine gas or liquefied fluorine would presumably be extremely destructive."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds are not within three times the permissible exposure limit, fluorine is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for fluorine had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid fluorine, and to prevent skin from becoming frozen from contact with vessels containing liquid fluorine.
- Where there is any possibility of exposure of an employee's body to liquid fluorine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid fluorine should be removed immedi-

ately and not reworn until the fluorine is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid fluorine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid fluorine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid fluorine should be immediately washed or showered to remove any fluorine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to fluorine may occur and control methods which may be effective in each case:

Operation	Controls
Use during organic and inorganic synthesis in the production of fluorine compounds, refrigerants, plastics, incendiary devices, and electrolytic solvents	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a rocket fuel oxidizer for ammonia, hydrazine, hydrogen, JP-4, and diborane fuels at laboratories and test sites	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid fluorine or high concentrations of fluorine gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid fluorine or high concentrations of fluorine gas get on the skin, immediately flush the contaminated skin with water. If liquid fluorine or high concentrations of fluorine gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of fluorine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If fluorine is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

REFERENCES

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RESPIRATORY PROTECTION FOR FLUORINE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 25 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against fluorine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of fluorine; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 25 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Fluorotrichloromethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CCl_3F
- Synonyms: Refrigerant 11; Freon 11; monofluorotrichloromethane; trichlorofluoromethane; trichloromonofluoromethane
- Appearance and odor: Colorless liquid or gas with a chlorinated-solvent odor that is detectable only at concentrations well above the permissible exposure (above 20% by volume).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluorotrichloromethane is 1000 parts of fluorotrichloromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5600 milligrams of fluorotrichloromethane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for fluorotrichloromethane from 1000 ppm as a time-weighted average value to 1000 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Fluorotrichloromethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Fluorotrichloromethane may cause drowsiness, unconsciousness, and death. Breathing high concentrations of this material may also cause the heart to beat irregularly or to stop suddenly.

2. Long-term Exposure: Prolonged overexposure to fluorotrichloromethane may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to fluorotrichloromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to fluorotrichloromethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from fluorotrichloromethane exposure.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of fluorotrichloromethane might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Fluorotrichloromethane vapor is a narcotic and may cause asphyxia at high concentrations. The approximate lethal concentration for rats exposed for 4 hours was 66,000 ppm; guinea pigs exhibited stupor and incoordination after exposure to 50,000 ppm for 2 hours, while animals breathing concentrations of 22,000 ppm showed only occasional tremors. Repeated exposure of several species to 4,000 ppm for 7 hours daily resulted in no toxic effects. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest,

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probably due to sensitization of the myocardium. No instances of toxic effects from industrial exposure have been reported, but since the substance can dissolve the natural oils of the skin, dermatitis may be expected to result from repeated contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 137.4
  2. Boiling point (760 mm Hg): 23.8 C (74.8 F)
  3. Specific gravity (water = 1): 1.49
  4. Vapor density (air = 1 at boiling point of fluorotrichloromethane): 4.7
  5. Melting point: −111 C (−168 F)
  6. Vapor pressure at 20 C (68 F): 690 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.11
  8. Evaporation rate (butyl acetate = 1): 63
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Fluorotrichloromethane reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when fluorotrichloromethane decomposes.
  4. Special precautions: Liquid fluorotrichloromethane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

According to Patty, fluorotrichloromethane is odorless; therefore, for the purposes of this guideline, it is treated as a material with poor warning properties. Fluorotrichloromethane is not a known eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for fluorotrichloromethane had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid fluorotrichloromethane.
- Non-impervious clothing which becomes wet with liquid fluorotrichloromethane should be removed promptly and not reworn until the fluorotrichloromethane has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid fluorotrichloromethane may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to fluorotrichloromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a propellant in aerosols for insecticides, floor waxes, paint, cosmetics, and perfumes	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a refrigerant; as a blowing agent in foam plastics; as a solvent and degreaser; in production of polymeric	General dilution ventilation; local exhaust ventilation; personal protective equipment

resins; as a dielectric fluid in bubble chambers, and in wind tunnels; use as a sulfonation solvent in chemical synthesis

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid fluorotrichloromethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid fluorotrichloromethane gets on the skin, immediately flush the contaminated skin with water if the liquid fluorotrichloromethane has already evaporated. If liquid fluorotrichloromethane soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of fluorotrichloromethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention immediately.

- **Swallowing**

When fluorotrichloromethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If fluorotrichloromethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow of gas.
3. If in the liquid form, allow to vaporize.

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RESPIRATORY PROTECTION FOR FLUOROTRICHLOROMETHANE

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR FORMALDEHYDE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about formaldehyde for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** CH_2O
- **Structure:** $CH_2{=}O$
- **Synonyms:** Formalin, methanal, methyl aldehyde, methylene glycol, methylene oxide, morbicid, paraform, superlysoform
- **Identifiers:** CAS 50-00-0; RTECS LP8925000; DOT 1198 and 2209, label required: "Combustible Liquid"
- **Appearance and odor:** Colorless gas with a pungent and irritating odor at ambient temperatures; also, commercially available at 30% to 55% formaldehyde in aqueous solution (formalin)

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 30.03
2. Boiling point (at 760 mmHg): -19.5°C (-3.06°F); 98°C (208°F) for 37% formaldehyde (15% methanol)
3. Specific gravity at 20°C (water = 1): 0.815; 1.075-1.081 for 37% formaldehyde (15% methanol)
4. Vapor density (air = 1 at boiling point of formaldehyde): 1.07
5. Melting point: -92°C (-133.5°F); -15°C (5°F) for 37% formaldehyde (15% methanol)
6. Vapor pressure at -88°C (-126.3°F): 10 mmHg
7. Soluble in water
8. Ionization potential: 10.88 eV

- **Reactivity**

1. Incompatibilities: Formaldehyde reacts violently with strong oxidants and alkaline materials.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving formaldehyde.
3. Caution: Formaldehyde should not be stored in confined spaces or near open flames, and containers should be protected from physical damage. Formaldehyde may react with hydrogen chloride to form bis-chloromethyl ether, a carcinogen.

- **Flammability**

1. Flash point: 50°C (122°F) for 37% formaldehyde (15% methanol) (closed cup); 85°C (185°F) for 37% formaldehyde (methanol free) (closed cup)
2. Autoignition temperature: 430°C (806°F) for 37% formaldehyde (methanol free)
3. Flammable limits in air, % by volume: Lower, 7; upper, 73
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide, or water spray (mist)
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA) for 37% formaldehyde (15% methanol); Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA) for 37% formaldehyde (methanol free)

- **Warning properties**

1. Odor threshold: 0.8 ppm
2. Eye irritation levels: In acclimated workers, mild to unpleasant irritation occurs at 2-10 ppm, and intolerable irritation (tissue damage possible) occurs at levels above 25 ppm.
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for formaldehyde is 1 part of formaldehyde per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the OSHA short-term exposure limit (STEL) is 2 ppm for any 15-minute sampling period (see 29 CFR 1910.1048). The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 0.016 ppm [0.02 milligram of formaldehyde per cubic meter of air (mg/m^3)] as an 8-hour TWA and 0.1 ppm (0.15 mg/m^3) as a ceiling concentration determined in any 15-minute sampling

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period. This REL represents the lowest reliably quantifiable concentration at the present time. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated formaldehyde as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 1 ppm (1.5 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 2 ppm (3 mg/m^3) (Table 1).

Table 1.—Occupational exposure limits for formaldehyde

	Exposure Limits	
	ppm	mg/m^3
OSHA PEL TWA	1	—
STEL (15 min)	2	—
NIOSH REL TWA (Ca)*	0.016	0.02
Ceiling (15 min)	0.1	0.12
ACGIH TLV® TWA (A2)†	1	1.5
STEL (A2)	2	3

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Formaldehyde may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Chronic inhalation of formaldehyde by rats produced cancer of the nasal cavity.
2. *Effects on humans:* Acute inhalation of formaldehyde has caused bronchitis, pulmonary edema, pneumonitis, pneumonia, and death due to respiratory failure. Formaldehyde solutions have caused eye burns, permanent corneal opacification, and loss of vision.

Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to formaldehyde gas can cause irritation of the eyes and respiratory tract, tearing, coughing, dry throat, tightening of the chest, headache, sensation of pressure in the head, and palpitations of the heart. Ingestion of formaldehyde can cause irritation of the mouth, throat, and stomach, nausea, vomiting, convulsions, and coma.
2. *Long-term (chronic):* Exposure to formaldehyde can cause dermatitis and sensitization of the skin and respiratory tract.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to formaldehyde, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to formaldehyde. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or of chronic skin disease, concurrent dermatitis, and significant breathing impairment due to preexisting chronic lung disease. Skin patch testing with formaldehyde is *not* recommended because of the risk of sensitization.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to formaldehyde. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and pre- and post-shift tests of lung function. Because formaldehyde gas is rapidly metabolized to naturally occurring compounds in the nasopharyngeal tissues and therefore does not accumulate in the blood, biologic monitoring would not be effective in detecting the presence of formaldehyde or its metabolites in the blood or urine.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to formaldehyde may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Extrinsic asthma and allergic and/or contact dermatitis.
2. Delayed-onset SHE's include: Extrinsic asthma.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to formaldehyde should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations. of formaldehyde. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting formaldehyde with solid sorbent tubes filled with 2-(benzylamino) ethanol on Chromosorb 102 or XAD-2, followed by desorption with isooctane, ultrasonic bath, or shaking, and analyzing by using a gas chromatograph with a hydrogen-air flame ionization detector. Direct reading devices calibrated to measure formaldehyde may also be used if available. A detailed sampling and analytical method for formaldehyde may be found in the *NIOSH Manual of Analytical Methods* (method number 2502).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with formaldehyde.

SANITATION

Clothing which is contaminated with formaldehyde should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of formaldehyde from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of formaldehyde's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with formaldehyde should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle formaldehyde should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to formaldehyde may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for formaldehyde

Operations	Controls
During the synthesis and handling of formaldehyde resins; during the synthesis of chelating agents and dyes	Process enclosure, local exhaust ventilation, personal protective equipment
During use in textile manufacturing and handling and in tanning operations	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of particle board, soft wood plywood, sandpaper, and grinding wheels	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an embalming fluid	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to formaldehyde, an eye-wash fountain should be provided within the immediate work area for emergency use.

If formaldehyde gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to formaldehyde, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If formaldehyde gets on the skin, wash it immediately with soap and water. If formaldehyde penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If formaldehyde is spilled or leaked, the following steps should be taken:

1. If formaldehyde is in the gaseous form, stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing formaldehyde, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing formaldehyde may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
6. Liquids containing formaldehyde may be collected by vacuuming with an appropriate system. If a vacuum system is used to remove formaldehyde, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic enviromental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for formaldehyde

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Formic Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HCOOH
- Synonyms: Formic acid 85%; formic acid 90%; formic acid 95%; hydrogen carboxylic acid; methanoic acid
- Appearance and odor: Colorless liquid that may fume with a pungent, penetrating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for formic acid is 5 parts of formic acid per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9 milligrams of formic acid per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Formic acid can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Formic acid may cause irritation of the eyes, nose, throat, upper respiratory tract, and skin. These are often accompanied by watering of the eyes, nasal discharge, and coughing. Skin contact with concentrated solutions causes severe irritation and blistering. Swallowing formic acid has caused a number of cases of severe poisoning and death. The symptoms found in this type of poisoning include salivation, vomiting, burning sensation of the mouth, bloody vomiting, diarrhea, and pain. In severe poisoning, the person may go into shock. Later, the person may have trouble breathing and may die. The person may also have kidney damage. One death has been reported in a worker who had hot formic acid splashed in his face. This worker could not speak, had trouble breathing, and died six hours later.

2. Long-term Exposure: Prolonged or repeated exposure to formic acid may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to formic acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to formic acid at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from formic acid exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of formic acid might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Formic acid is a primary skin irritant and has caused skin sensitization. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although formic acid is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Liver disease: Although formic acid is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Eye disease: Formic acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Formic acid vapor is a severe irritant of the eyes, mucous membranes, and skin. Exposure causes eye irritation with lacrimation, nasal discharge, throat irritation, and cough. A worker splashed in the face with hot formic acid developed marked dyspnea with dysphagia, and died within 6 hours. Workers exposed to a mixture of formic and acetic acids at an average concentration of 15 ppm of each complained of nausea. The liquid on the skin causes burns with vesiculation; keloid formation at the site of the burn often results. Skin sensitization may occur in persons previously exposed to formaldehyde. While ingestion of the liquid is unlikely in ordinary industrial use, the highly corrosive nature of the substance may be expected to produce serious burns of the mouth and esophagus.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46.03
2. Boiling point (760 mm Hg): 85%: 107 C (224.6 F); 90%: 106.5 C (223.7 F); 95%: 102 C (215.6 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of formic acid): 1.6
5. Melting point: 85%: −15.3 C (4.5 F); 90%: −6.5 C (20.3 F); 95%: 1.4 C (34.5 F)
6. Vapor pressure at 20 C (68 F): 23− 33 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 2.1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers or strong caustics may cause fires and explosions. Contact with concentrated sulfuric acid causes formation of toxic and flammable carbon monoxide gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving formic acid.
4. Special precautions: Liquid formic acid will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point (90% solution): 50 C (122 F) (closed cup)
2. Autoignition temperature (90% solution): 435 C (813 F)
3. Flammable limits in air, % by volume: Lower: 18; Upper: 57
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold of 21 ppm. Patty states that formic acid has a "pungent, penetrating" odor.
2. Eye Irritation Level: Grant notes,'It has been said that the vapors of formic acid are irritating to the eyes . . ., but there appears to be little in the literature on this subject." According to Patty, "the principal hazard is that of severe primary damage to the skin, eye, or mucosal surfaces." Deichmann and Gerarde also state that formic acid is irritating to the eyes.
3. Other Information: Grant, Patty, and Deichmann and Gerarde report that formic acid is a mucous membrane irritant, capable of irritating the upper respiratory tract and the eyes. The *Documentation of TLV's* states that "workers exposed to formic and acetic acids in a textile plant . . . at concentrations of each acid averaging 15 ppm" experienced irritation at these levels.
4. Evaluation of Warning Properties: Through its odor and irritant effects, formic acid is detectable at concentrations only several times the permissible exposure limit. For the purposes of this guideline, therefore, formic acid is judged to have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of formic acid on chromosorb 103, desorption with deionized water, and analysis by ion chromatography. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure formic acid may be used. An analytical method for formic acid is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid formic acid.
- Clothing contaminated with formic acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of formic acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the formic acid, the person performing the operation should be informed of formic acid's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid formic acid, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with formic acid should be removed immediately and not reworn until the formic acid is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid formic acid or solutions containing formic acid contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid formic acid or solutions containing 1% or more of formic acid by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with formic acid should be immediately washed or showered to remove any formic acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to formic acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile dyeing and finishing industry as a dye exhausting agent; chrome dyeing; to impart finishes to cotton; an acidifying agent; and shrink- and wrinkle-proofing compound	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate as a strong reducing agent for acids, salts, dyes, fumigants, refrigerants, pharmaceuticals, and solvents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in leather processing industry as a deliming agent and neutralizer; as a preservative and levelling agent	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry as a coagulant for natural rubber latex and form making; as a preservative of latex	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst in hydrocarbon-formaldehyde resins and phenolic resins, and plasticizer for vinyl resins	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in electroplating industry to control particle size and plating thickness	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an antiseptic in wine and beer brewing, preservative in animal feed additives and cleaning solution compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous operations as a wire stripping compound and preparing bare wires for soldering; laundry sour; and as an oil well acidifying agent	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If formic acid or solutions containing formic acid get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If formic acid gets on the skin, immediately flush the contaminated skin with water. If formic acid soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of formic acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If formic acid has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the formic acid. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If formic acid is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Formic acid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Formic acid may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR FORMIC ACID

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor of Particulate Concentration	
100 ppm or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Furfural

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_4H_3OCHO
- Synonyms: 2-Furaldehyde; furfuraldehyde; fural; 2-furancarboxaldehyde
- Appearance and odor: Colorless to light brown liquid that darkens on standing in light and air. Odor is like almonds.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for furfural is 5 parts of furfural per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 20 milligrams of furfural per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for furfural from 5 ppm to 2 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Furfural can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Furfural may cause irritation of the skin, eyes, and respiratory tract. It may also cause a person to become unconscious.

2. Long-term Exposure: Furfural may cause sensitization of the skin, loss of sense of taste, and numbness of the tongue.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to furfural.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to furfural at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from furfural exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of furfural might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Skin disease: Furfural can cause dermatitis on excessive exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although furfural is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although furfural is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Furfural vapor is irritating to the eyes, respiratory tract, and skin. It has been reported to be a central nervous system poison in large doses in some animals, causing hyper-reflexia and convulsions.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 96
2. Boiling point (760 mm Hg): 162 C (323 F)
3. Specific gravity (water = 1): 1.16
4. Vapor density (air = 1 at boiling point of furfural): 3.3
5. Melting point: −36.5 C (−33.7 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.3
8. Evaporation rate (butyl acetate = 1): Very low

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong acids and oxidizing materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving furfural.
4. Special precautions: None

- **Flammability**

1. Flash point: 60 C (140 F) (closed cup)
2. Autoignition temperature: 316 C (600 F)
3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 19.3
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "although the odor threshold of furfural vapor has been reported to be 0.25 to 0.38 ppm, some industrial hygienists maintain that the odor becomes readily noticeable only near the TLV concentration of 5 ppm."
2. Eye Irritation Level: Grant states that "chronic exposure to the vapor at concentrations of 13.5 ppm or less in air is reported to cause reddening of the eyes, tearing, and irritation of the throat in workers." The *Hygienic Guide* states that the "irritating properties of furfural, which become uncomfortable at 20 to 50 ppm, probably preclude voluntary exposures which might lead to significant injury."
3. Nasal Irritation Level: The *Hygienic Guide* states that "nasal irritation would indicate that the TLV was being exceeded."
4. Evaluation of Warning Properties: Through its odor and irritant effects, furfural can be detected near the permissible exposure limit. For the purposes of this guideline, therefore, furfural is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for furfural is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid furfural.
- Clothing contaminated with furfural should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of furfural from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the furfural, the person performing the operation should be informed of furfural's hazardous properties.
- Non-impervious clothing which becomes contaminated with furfural should be removed promptly and not reworn until the furfural is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid furfural may contact the eyes.

SANITATION

- Skin that becomes contaminated with furfural should be promptly washed or showered to remove any furfural.
- Employees who handle liquid furfural should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to furfural may occur and control methods which may be effective in each case:

Operation	Controls
Use during removal of industrial coatings in open-surface tanks	Local exhaust ventilation; personal protective equipment
Liberation during cold molding of abrasive grinding wheels	General dilution ventilation
Use in rubber of phenolic cement adhesives	General dilution ventilation; personal protective equipment
Liberation during molding of miscellaneous phenolic resin products	Local exahaust ventilation; general dilution ventilation
Use during molding of friction materials as brake linings, clutch facings, brake blocks, etc.	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of reinforced plastic products	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during coating of products with resins/varnishes as wire coating, food containers, paper, canvas, etc.	General dilution ventilation; process enclosure; local exhaust ventilation
Liberaiton during vulcanization of rubber in processes using furfural as an accelerator	General dilution ventilation; process enclosure; local exhaust ventilation
Liberation during manufacture of furfuryl alcohol	Process enclosure; general dilution ventilation
Liberation during use as a chemical intermediate in manufacture of furor, tetrahydrofuran, tetrahydrofuryl alcohol, hexamethylene diamene, and pyromucic acid	General dilution ventilation
Liberation during manufacture of phenolic-furfural resins; during dewaxing of oils, primarily lubricating oils; during decolorization of wood resins	Process enclosure; general dilution ventilation
Use during manufacture of surface coatings	General dilution ventilation; process enclosure; local exhaust ventilation
Liberation during separation of butadiene, benzene, and miscellaneous compounds from C_4 hydrocarbons; during manufacture of some polyurethane elastomers	Process enclosure; general dilution ventilation
Use during in situ desludging and decarbonizing of internal combustion engines	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If furfural gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If furfural gets on the skin, promptly flush the contaminated skin with water. If furfural soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of furfural, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- Swallowing

When furfural has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If furfural is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. For large quantities, cover with sodium bisulfite ($NaHSO_3$), add a small amount of water and mix. Then, after one hour, flush with large amounts of water and wash site with soap solution.

- Waste disposal methods:

Furfural may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. For small quantities, by absorbing it in vermiculite, dry sand, earth, or a similar material and disposing it in a suitable combustion chamber.
3. For large quantities, by mixing with a flammable liquid (such as acetone) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR FURFURAL

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
250 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a fuil facepiece.
Greater than 250 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

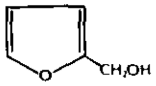
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR FURFURYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about furfuryl alcohol for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_5H_6O_2$
- **Structure:**



- **Synonyms:** 2-Furancarbinol, 2-furanmethanol, furfural alcohol, furyl alcohol, 2-furylcarbinol, 2-furylmethanol, 2-hydroxymethylfuran
- **Identifiers:** CAS 98-00-0; RTECS LU9100000; DOT 2874, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless to pale yellow, syrupy liquid with a mild odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.10
2. Boiling point (at 760 mmHg): 170°C (338°F)
3. Specific gravity (water = 1): 1.1351
4. Vapor density (air = 1 at boiling point of furfuryl alcohol): 3.38
5. Melting point: -14.63°C (5.7°F)
6. Vapor pressure at 31.8°C (89°F): 1 mmHg
7. Miscible with water
8. Evaporation rate (butyl acetate = 1): Very slow
9. Saturation concentration in air (approximate) at 31.8°C (89°F): 0.13% (1,300 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong acids (including some organic acids) or acid catalysts may cause polymerization with the liberation of heat and violent spattering. Avoid contact with strong oxidizers.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving furfuryl alcohol.
3. Caution: Furfuryl alcohol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 77°C (170°F) (closed cup)
2. Autoignition temperature: 490°C (915°F)
3. Flammable limits in air, % by volume: Lower, 1.8; Upper, 16.3
4. Extinguishant: Alcohol foam, carbon dioxide, or dry chemical
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 7-8 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, furfuryl alcohol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, furfuryl alcohol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for furfuryl alcohol is 50 parts of furfuryl alcohol per million parts of air (ppm) [200 milligrams of furfuryl alcohol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (200 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 10 ppm (40 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek; and the ACGIH short-term exposure limit (STEL) is 15 ppm (60 mg/m^3) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for furfuryl alcohol

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	50	200
NIOSH REL TWA	50	200
ACGIH TLV® TWA (Skin)*	10	40
STEL (Skin)	15	60

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• Routes of exposure

Furfuryl alcohol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of Toxicology

Effects on animals: Repeated daily exposure to mice, rats, or rabbits to furfuryl alcohol caused increased respiration, respiratory tract irritation, and vascular congestion, followed by decreased respiration, decreased force of cardiac contraction, decreased contractility of the gastrointestinal tract, drop in blood pressure, paralysis of sensory nerves, and death due to respiratory failure or possibly to cardiac arrest.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to furfuryl alcohol can cause excitement, drowsiness, nausea, vomiting, salivation, diarrhea, dizziness, shortness of breath, irregular breathing, and increased urination. Eye contact with furfuryl alcohol can cause redness, tearing, serious irritation, and corneal opacities; dermal contact can cause minor irritation.
2. *Long-term (chronic):* Exposure to furfuryl alcohol can cause headache, eye irritation, and dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to furfuryl alcohol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, cardiovascular, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to furfuryl alcohol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to furfuryl alcohol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and cardiovascular, nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to furfuryl alcohol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting furfuryl alcohol vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure furfuryl alcohol may also be used if available. A detailed sampling and analytical method for furfuryl alcohol may be found in the *NIOSH Manual of Analytical Methods* (method number S365).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with furfuryl alcohol.

Workers should be provided with and required to use splash-proof safety goggles where furfuryl alcohol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with furfuryl alcohol should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of furfuryl alcohol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of furfuryl alcohol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with furfuryl alcohol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle furfuryl alcohol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to furfuryl alcohol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for furfuryl alcohol

Operations	Controls
During the manufacture of cements, molded high-density carbon, and graphite articles; during the preparation of furfuryl-dimethylol urea and furan resins	Local exhaust ventilation, general exhaust ventilation, personal protective equipment
During the synthesis and handling of furfuryl alcohol; during use as a solvent; during use in impregnation of wood	Local exhaust ventilation, general exhaust ventilation, personal protective equipment
During use in sand consolidation for oil and gas recovery operations	General dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to furfuryl alcohol, an eye-wash fountain should be provided within the immediate work area for emergency use.

If furfuryl alcohol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to furfuryl alcohol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If furfuryl alcohol gets on the skin, wash it immediately with soap and water. If furfuryl alcohol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If furfuryl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities of liquids containing furfuryl alcohol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from furfuryl alcohol vapors. Burn the paper in a suitable location away from combustible materials.

4. Large quantities of liquids containing furfuryl alcohol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Furfuryl alcohol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for furfuryl alcohol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 250 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 50 ppm (200 mg/m^3) (TWA).

Occupational Health Guideline for Glycidol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_3H_6O_2$
- Synonyms: 2-Hydroxymethyloxiran; hydroxymethyl ethylene oxide; epoxypropyl alcohol; glycide; 3-hydroxypropylene oxide; 2,3-epoxy-1-propanol
- Appearance: Colorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for glycidol is 50 parts of glycidol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 150 milligrams of glycidol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Glycidol can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to glycidol may cause irritation of the eyes, nose, and throat.
2. *Long-term Exposure:* Prolonged overexposure might produce irritation of the skin.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to glycidol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to glycidol at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from glycidol exposure.

—Skin disease: Glycidol is a primary skin irritant and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of glycidol might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Glycidol vapor is an irritant to the eyes and upper respiratory tract, a skin irritant, and a central nervous system depressant. The LC50 for mice (4 hr) was 450 ppm, and for rats (8 hr), 580 ppm, resulting in pneumonitis; rats exposed at 400 ppm daily showed only slight eye irritation and mild respiratory distress, with no evidence of systemic toxicity. Lethal doses of 0.45 to 0.85 g/kg of the liquid administered by gastric tube resulted initially in nervous system depression, but surviving animals showed a reversal of the depressant effect, manifested by excitation and tremors. Direct application of the liquid to the skin of animals classifies glycidol as a moderate skin irritant; instilled into the eye, it is classified as a severe eye irritant. Exposure to near-saturated vapor for 8 hours resulted in corneal opacity. Repeated intramuscular injections do not affect hematopoiesis in rats. The only report of toxic effects in humans is that of irritation of the eyes, nose, and respiratory tract of experimenters working with the compound at room temperature.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74
2. Boiling point (760 mm Hg): 166 C (331 F) (decomposes)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of glycidol): 2.6
5. Melting point: −45 C (−49 F)
6. Vapor pressure at 20 C (68 F): 0.9 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents (especially nitrates) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving glycidol.
4. Special precautions: Glycidol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 72 C (162 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

1. Odor Threshold: No information is available concerning the odor threshold of glycidol.
2. Eye Irritation Level: Grant states, "In vapor form, glycidol has proven damaging to the corneas of rats, but for human beings the vapor has been found to have adequate warning properties, consisting of eye and respiratory irritation, to preclude excessive industrial exposure." The *Documentation of TLV's* states that following the first few exposures, "rats exposed at 400 ppm glycidol 7 hours a day for 50 days . . . (experienced) very slight irritation of the eyes, with slight lacrimation and encrustation of the eyelids . . . ." No quantitative information is available concerning the threshold of eye irritation.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of glycidol, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of glycidol vapors using an adsorption tube with subsequent desorption with tetrahydrofuran and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure glycidol may be used. An analytical method for glycidol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid glycidol.
- Clothing contaminated with liquid glycidol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of glycidol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the glycidol, the person performing the operation should be informed of glycidol's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid glycidol should be removed promptly and not reworn until the glycidol is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid glycidol may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid glycidol should be promptly washed or showered to remove any glycidol.
- Employees who handle liquid glycidol should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to glycidol may occur and control methods which may be effective in each case:

Operation	Controls
Use in surface coatings; use in chemical synthesis; use as a stabilizer for natural oils and vinyl polymers	General dilution ventilation; personal protective equipment
Use as a demulsifying agent; use as a dye leveling (retarding) agent	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If glycidol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If glycidol gets on the skin, promptly wash the contaminated skin with water. If glycidol soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of glycidol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When glycidol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If glycidol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber, or absorbed in vermiculite, dry sand, earth, or a similar material and disposed in a sanitary landfill.

- Waste disposal method:

Glycidol may be disposed of by dissolving in petroleum and atomizing in a suitable combustion chamber, or absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a sanitary landfill.

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RESPIRATORY PROTECTION FOR GLYCIDOL

Condition	**Minimum Respiratory Protection* Required Above 50 ppm**
Vapor Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Natural Graphite

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C
- Synonyms: Plumbago; potelot; carbo mineralis; black lead; carburet of iron; silver lead; crayon noir
- Appearance and odor: Black, greasy, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for natural graphite is 15 million particles of natural graphite per cubic foot of air (mppcf) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Natural graphite can affect the body if it is inhaled or if it comes in contact with the eyes.

- ***Effects of overexposure***

Repeated inhalation of natural graphite over a number of years may cause scarring of the lungs with such symptoms as chest tightness, shortness of breath, cough, black sputum, and pain.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to natural graphite.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to natural graphite at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system and the cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Natural graphite may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Natural graphite is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Natural graphite dust causes graphite pneumoconiosis. The earliest roentgenologic changes may be the disappearance of normal vascular markings, with the appearance later of pinpoint and macronodular densities in all lung fields. Massive lesions, when present, are caused by large cysts filled with black fluid. The pleura is often involved: hydrothorax, pneumothorax, and pleural thickening may occur. At autopsy, the lungs are gray-black to black; histologically there are widely scattered particles, spicules, and plates of graphite, often within intra-alveolar phagocytes amidst diffuse interstitial fibrosis and occasionally pneumonitis. There are also interwoven bands of collagen, similar to those found in silicosis, which frequently are the most prominent feature of the fibrotic lesions occupying the lung and the bronchial lymph nodes. Symptoms include expectoration of black sputum, dyspnea, and cough. It has been generally believed that the capacity of inhaled natural graphite dust to cause disease is largely the result of its crystalline silica component. However, there is a recent report of a worker who, after exposure to "nearly pure" carbon for 17 years as a grinder of synthetic graphite bars, developed cough, dyspnea, and reduced pulmonary function, and died. At autopsy, both ventricles of

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the heart were hypertrophied, and the lungs revealed the typical findings of graphite pneumoconiosis including fibrous tissue; the ashed material from the lung showed little or no birefringent particles, indicating the absence of silicious material.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 12
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.25
  4. Vapor density (air = 1 at boiling point of natural graphite): Not applicable
  5. Melting point: 3350 C (6040 F) (sublimes)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with very strong oxidizers such as fluorine, chlorine trifluoride, and potassium peroxide may cause fires and explosions.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Flash point: Not applicable
  2. Minimum ignition temperature: 730 C (1346 F) (cloud); 580 C (1076 F) (layer)
  3. Minimum explosive concentration: Data not available
  4. Extinguishant: Water
- **Warning properties**

Grant states that "carbon, when pure, has no toxic effect on the eye. As superficial foreign bodies, carbon black and graphite may be slightly irritating mechanically and may cause discoloration of lids and conjunctivae, but they are chemically inert."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for graphite had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to natural graphite may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining, purification, packaging, blasting, and drilling	Local exhaust ventilation; personal protective equipment
Use in foundry facings; steelmaking as carbon raiser; manufacture of refractories in crucibles and retorts; use in manufacture of lubricants and adhesives in bearings, slides, gears, engines, and mold release agents	Process enclosure; local exhaust ventilation; personal protective equipment
Manufacture of writing and drafting agents; manufacture of industrial paints, inks, and polishes; manufacture of motor and generator brushes, batteries, carbon resistors, and electrodes	Process enclosure; local exhaust ventilation; personal protective equipment

Use in manufacture of tungsten carbide cutting tools, friction materials and clutch facings; use in electroplating; use in manufacture of ammunition; miscellaneous uses in hard rubber, engine packing, cord, rope, twine, floor coverings, and coatings for fertilizer	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If natural graphite gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Breathing**

If a person breathes in large amounts of natural graphite, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If natural graphite is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation, burning in a suitable combustion chamber or for disposal in a secured sanitary landfill.

- Waste disposal methods:

Natural graphite may be disposed of:

1. In a sanitary landfill.
2. By burning in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR NATURAL GRAPHITE

Condition	**Minimum Respiratory Protection* Required Above 15 mppcf**
Particulate Concentration	
75 mppcf or less	Any dust respirator.
150 mppcf or less	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mppcf or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7500 mppcf or less	A powered air-purifying respirator with a high efficiency filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7500 mppcf or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Hafnium and Compounds (as Hafnium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all hafnium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Hafnium

- Formula: Hf
- Synonyms: Hafnium, metallic; hafnium, elemental
- Appearance: Gray solid

Hafnium tetrachloride

- Formula: $HfCl_4$
- Synonyms: None
- Appearance and odor: White solid with an acrid odor in moist air.

Hafnium oxychloride

- Formula: $HfOCl_2 \cdot 8H_2O$
- Synonyms: Hafnium oxychloride octahydrate
- Appearance and odor: White, odorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hafnium and compounds (as hafnium) is 0.5 milligram of hafnium and compounds (as hafnium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hafnium, hafnium tetrachloride, or hafnium oxychloride can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Exposure to hafnium salts has caused irritation of the eyes and skin in animals. Hafnium chloride has caused liver damage in animals on prolonged feeding.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hafnium and compounds (as hafnium).

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to hafnium and compounds at potentially hazardous levels. The employer should screen employees for history of liver disease. Hafnium compounds have been reported to cause liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function. Only those giving a postive history of these conditions should be referred for further medical examinations.

- **Summary of toxicology**

Hafnium and its compounds have been reported to cause liver damage in animals. The LD50 of hafnium, chiefly as the oxychloride, was 76 mg Hf/kg for mice. A 90-day hafnium chloride feeding study in rats at 1.0% and 0.1% resulted in unspecified liver effects. Studies with radioactive Hf mandelate indicate slow elimination from the body. Some compounds may cause irritation of eyes, skin, and mucous membranes.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Hafnium**

1. Molecular weight: 178.5
2. Boiling point (760 mm Hg): 3100 C (5612 F) approximately
3. Specific gravity (water = 1): 13.3
4. Vapor density (air = 1 at boiling point of hafnium): Not applicable
5. Melting point: 2227 C (4040 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data —Hafnium tetrachloride**

1. Molecular weight: 320.3
2. Boiling point (760 mm Hg): 317 C (603 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of hafnium tetrachloride): Not applicable
5. Melting point: 432 C (809 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Hafnium oxychloride**

1. Molecular weight: 409.5
2. Boiling point (760 mm Hg): Decomposes (data not available)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of hafnium oxychloride): Not applicable
5. Melting point: Less than 50 C (less than 122 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of hafnium metal with chlorine and strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving hafnium, hafnium tetrachloride, or hafnium oxychloride.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Hafnium: Data not applicable; hafnium tetrachloride and hafnium oxychloride: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Hafnium: Water; hafnium tetrachloride and hafnium oxychloride: Not applicable

- **Warning properties**

Hafnium is not known to be an eye irritant; however, Haley reports that hafnium compounds may prove irritating to the mucosal surfaces.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for hafnium and compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with wet or dry hafnium powder. The clothing should be flame-resistant and should be treated or should be of a type so as to minimize the static electricity hazard of ignition.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

*necessary to prevent skin contact with hafnium tetra*chloride, hafnium oxychloride, or liquids containing these compounds, where skin contact may occur.

- If employees' clothing has had any possibility of *being contaminated with* wet or dry *hafnium* powder, employees should change into uncontaminated clothing before leaving the work premises.
- If employees' clothing may have become contaminated with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with wet or dry hafnium powder should be placed in fireproof closed containers for storage until it can be discarded or until provision is made for the removal of hafnium from the clothing. If the clothing is to be laundered or *otherwise cleaned to remove the* hafnium, the person performing the operation should be informed of hafnium's hazardous properties.
- Clothing contaminated with hafnium tetrachloride or hafnium oxychloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to wet or dry hafnium powder, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where exposure of an employee's body to hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes contaminated with wet or dry hafnium powder should be removed promptly but in a careful and cautious manner so as to reduce the probability of ignition by friction, static electricity, or other causes. Such clothing should not be reworn until the hafnium is removed from the clothing.
- Non-impervious clothing which becomes wet with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds should be removed promptly and not reworn until the contaminant is *removed from the clothing.*
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of wet or dry hafnium powder, hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to wet or dry hafnium powder, hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with wet or dry hafnium powder should wash any areas of the body which may have contacted hafnium powder at the end of each work day.
- Skin that becomes wet with wet or dry hafnium powder should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.
- Skin that becomes contaminated with hafnium tetrachloride, hafnium oxychloride, or liquids these compounds should be promptly washed or showered to remove any contaminant.
- Eating and smoking should not be permitted in areas where wet or dry hafnium powder, hafnium tetrachlo*ride, or solid hafnium oxychloride or liquids containing* these compounds are handled, processed, or stored.
- Employees who handle hafnium or its compounds or liquids containing hafnium or its compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hafnium and compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining and purification of hafnium (separation from zirconium); manufacture and fabrication of special alloys	Local exhaust ventilation; personal protective equipment
Use as control rods in water-cooled nuclear reactors; use in gas-filled tubes and incandescent lamps as scavenger for oxygen and nitrogen; use in the manufacture of photographic flash bulbs, light bulb filaments, and in *electronic equipment* as cathodes and capacitors	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If hafnium, hafnium tetrachloride, or hafnium oxychloride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If hafnium gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If hafnium tetrachloride or hafnium oxychloride get on the skin, promptly flush the contaminated skin with water. If hafnium or its compounds soak through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of hafnium, hafnium tetrachloride, or hafnium oxychloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When hafnium, hafnium tetrachloride, or hafnium oxychloride have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If hafnium, hafnium tetrachloride, or hafnium oxychloride are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing hafnium, hafnium tetrachloride, or hafnium oxychloride should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Hafnium, hafnium tetrachloride, or hafnium oxychloride may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR HAFNIUM AND COMPOUNDS (AS HAFNIUM)

Condition	**Minimum Respiratory Protection* Required Above 0.5 mg/m³**
Particulate Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.
5 mg/m³ or less	Any dust and mist respirator, except single-use respirator or quarter mask. Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 250 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Heptachlor *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_5Cl_7$ (principal ingredient)
- Synonyms: 1,4,5,6,7,8,8a-Heptachloro-3a,4,7,7a-tetra-hydro-4, 7-methanoindene (principal ingredient)
- Appearance and odor: Light tan, waxy solid with an odor like camphor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for heptachlor is 0.5 milligram of heptachlor per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Heptachlor can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

In animals, exposure to heptachlor has produced tremors, convulsions, and liver damage. Heptachlor is very similar to chlordane. Exposure to chlordane has caused convulsions and kidney damage in humans.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to heptachlor.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to heptachlor at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders would be expected to be at increased risk from exposure. Examination of the eyes, nervous system, liver, and kidneys should be stressed.

2. Periodic Medical Examination: The aforementioned medical examination should be repeated on an annual basis.

- **Summary of toxicology**

Heptachlor dust is a convulsant in animals. In rats the oral LD50 was 90 mg/kg; within 30 to 60 minutes after administration there were tremors and convulsions; liver damage occurred. Multiple applications of a solution to the skin of rats of 20 mg/kg were toxic, indicating a marked cumulative action. The carcinogenicity of heptachlor was tested in rats by oral administration; one of five experiments suggested hepatocarcinogenicity, but this was not reproduced in the other experiments within the same dose range. Rats given heptachlor in the diet at 6 mg/kg body weight developed cataracts after 4.5 to 9.5 months of feeding. In animals, heptachlor is more potent than chlordane, to which it is closely related chemically; ingestion of chlordane has caused convulsions and kidney damage in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 373.5 (principal ingredient)
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.65
  4. Vapor density (air = 1 at boiling point of heptachlor): Not applicable
  5. Melting point: 46 – 74 C (114 – 165 F)
  6. Vapor pressure at 20 C (68 F): 0.0003 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F):

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Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Solid: None. Liquid (above 74 C (165 F): Can react with iron and rust to form toxic hydrogen chloride gas.

2. Incompatibilities: Contact of melted heptachlor with iron and rust may form hydrogen chloride gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when heptachlor decomposes.

4. Special precautions: None.

- **Flammability**

1. Not combustible, but may be dissolved in flammable liquid

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of heptachlor.

2. Eye Irritation Level: Heptachlor is not known to be an eye irritant.

3. Evaluation of Warning Properties: Since there is no quantitative information available relating warning properties to air concentrations of heptachlor, it has been treated as a material with poor warning properties. Its concentration in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for heptachlor is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with heptachlor or liquids containing heptachlor where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with heptachlor or liquids containing heptachlor, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with heptachlor should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of heptachlor from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the heptachlor, the person performing the operation should be informed of heptachlor's hazardous properties.
- Where exposure of an employee's body to heptachlor or liquids containing heptachlor may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with heptachlor should be removed immediately and not reworn until the heptachlor is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where heptachlor or liquids containing heptachlor may contact the eyes.

SANITATION

- Skin that becomes contaminated with heptachlor should be immediately washed or showered with soap or mild detergent and water to remove any heptachlor.
- Workers subject to skin contact with heptachlor or liquids containing heptachlor should wash with soap or mild detergent and water any areas of the body which may have contacted heptachlor at the end of each work day.
- Eating and smoking should not be permitted in areas where heptachlor or liquids containing heptachlor are handled, processed, or stored.
- Employees who handle heptachlor or liquids contain-

ing heptachlor should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to heptachlor may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticides supplied as an emulsifiable concentrate, wettable powder, dust or granular material	Local exhaust ventilation; personal protective equipment; general dilution ventilation
Use as an insecticide in seed treatment, preplanting soil application, dipping tops of plants and roots for control of insects, flies and mosquitoes; use on household plots and on agricultural crops and fruits; use in termite control (dispensed in caulking guns)	Personal protective equipment
Manufacture of heptachlor	*Process enclosure; local exhaust ventilation; personal protective equipment*

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If heptachlor or liquids containing heptachlor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If heptachlor or liquids containing heptachlor get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If heptachlor or liquids containing heptachlor soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of heptachlor, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When heptachlor or liquids containing heptachlor have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If heptachlor is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing heptachlor should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Heptachlor may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 5, 1974.

RESPIRATORY PROTECTION FOR HEPTACHLOR

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
5mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
700 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 700 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of heptachlor; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 700 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure moae should also be worn.

Occupational Health Guideline for Heptane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3(CH_2)_5CH_3$
- Synonyms: Normal heptane
- Appearance and odor: Colorless liquid with a mild, gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for heptane is 500 parts of heptane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of heptane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 85 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 440 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Heptane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to heptane may cause a slight irritation of the eyes, nose, and throat, lightheadedness, hilarity, semi-consciousness, and dizziness. It may also cause loss of appetite and nausea. Higher concentrations may cause unconsciousness.

2. Long-term Exposure: Prolonged overexposure to the liquid may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to heptane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to heptane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Heptane is a skin defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of heptane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although heptane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although heptane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: The aforementioned examinations should be performed on an annual basis.

- **Summary of toxicology**

Heptane vapor is a narcotic. Concentrations of 10,000 to 15,000 ppm produced narcosis in mice within 30 to 60 minutes, while 15,000 to 20,000 ppm caused convulsions

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and death. At 48,000 ppm respiratory arrest was produced in mice in 3 to 4 minutes from the start of exposure. Human subjects exposed to 1000 ppm for 6 minutes, or to 2000 ppm for 4 minutes, reported slight vertigo. At 5000 ppm for 4 minutes, there was marked vertigo, inability to walk a straight line, hilarity, and incoordination, but no complaints of eye and upper respiratory tract or mucous membrane irritation. A 15-minute exposure at 5000 ppm produced in some subjects a state of stupor lasting for 30 minutes after exposure. These subjects also reported loss of appetite, slight nausea, and a taste resembling gasoline for several hours after exposure. The liquid is a defatting agent, and prolonged exposure may cause irritation of the skin. Aspiration may cause a chemical pneumonia. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): 98.4 C (209 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of heptane): 3.5
5. Melting point: −90.6 C (−132 F)
6. Vapor pressure at 20 C (68 F): 40 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.005
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving heptane.
4. Special precautions: Heptane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −3.9 C (25 F) (closed cup)
2. Autoignition temperature: 215 C (419 F)
3. Flammable limits in air, % by volume: Lower: 1.05; Upper: 6.7
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Summer reports an odor threshold of 220 ppm; May reports 50 and 220 ppm.
2. Eye Irritation Level: Heptane is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of heptane is well below the permissible exposure limit, heptane is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of heptane. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of heptane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure heptane may be used. A analytical method for heptane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid heptane.
- Any clothing which becomes wet with liquid heptane should be removed immediately and not reworn until the heptane is removed from the clothing.
- Clothing wet with liquid heptane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of heptane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the heptane, the person performing the operation should be informed of heptane's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid heptane may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to heptane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid heptane should be promptly washed or showered with soap or mild detergent and water to remove any heptane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to heptane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a carrier and penetrant solvent for adhesives, use in azeotrophic distillations, and in rubber tire manufacture; as a solvent in rubber cements	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an ink solvent in gravure printing	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent in polymer industry as a swelling and blowing agent for plastic foams	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a reference fuel for testing gasoline engine knock and pollution and combustion studies	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a diluent solvent for lacquers during preparation and application	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic chemical synthesis in preparations of toluene and alkylbenzenes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an extraction solvent for tallow from meat, rosin from wood, and oils from seeds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cleaning surfaces before application of adhesives	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a laboratory solvent for scientific testing	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If heptane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If heptane gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If heptane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of heptane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If heptane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If heptane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Heptane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Heptane may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR HEPTANE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
850 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
4250 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 4250 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Hexachloroethane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CCl_3CCl_3
- Synonyms: Perchloroethane
- Appearance and odor: Colorless solid with a camphor-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hexachloroethane is 1 part of hexachloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 10 milligrams of hexachloroethane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for hexachloroethane from 1 ppm to 10 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hexachloroethane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

Exposure to the hot fumes of hexachloroethane may cause irritation of the eyes.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hexachloroethane. employee who is exposed to hexachloroethane at potentially hazardous levels.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to hexachloroethane at potentially hazardous levels.

- **Summary of toxicology**

Hexachloroethane is an eye irritant. High oral doses in animals cause hepatic, renal, and central nervous system effects. Dogs given oral doses of 1 to 1.4 g/kg showed depression of the central nervous system characterized by weakness, staggering, and muscle twitching. When administered orally to domestic animals as a parasiticide, it caused chronic lesions in the liver and acute, diffuse nephrosis in cattle at high doses, but it had no noticeable toxic effect in horses at levels of 0.2 g/kg. Exposure of workmen to fumes from hot hexachloroethane resulted in blepharospasm, photophobia, lacrimation, and reddening of the conjunctiva, but no corneal injury or permanent damage. No chronic effects have been reported from industrial exposure, although significant absorption through the skin is said to occur.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 236.7
  2. Boiling point (760 mm Hg): 189 C (372 F) (sublimes)
  3. Specific gravity (water = 1): 2.1
  4. Vapor density (air = 1 at boiling point of hexachloroethane): 8.2
  5. Melting point: 189 C (372 F) (sealed tube)
  6. Vapor pressure at 20 C (68 F): 0.22 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.005
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**

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1. Conditions contributing to instability: Heat

2. Incompatibilities: Hexachloroethane reacts with hot iron, zinc, and aluminum. Dehalogenation by reaction with alkalies will produce spontaneously explosive chloroacetylene.

3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, chlorine, carbon tetrachloride, and tetrachloroethylene) may be released when hexachloroethane decomposes.

4. Special precautions: Liquid hexachloroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Although hexachloroethane has a camphor-like odor, no quantitative data are available relating air concentrations of this substance to warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of hexachloroethane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hexachloroethane may be used. An analytical method for hexachloroethane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid hexachloroethane or liquids containing hexachloroethane.
- If employees' clothing may have become contaminated with solid hexachloroethane or liquids containing hexachloroethane, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with solid hexachloroethane or liquids containing hexachloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hexachloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hexachloroethane, the person performing the operation should be informed of hexachloroethane's hazardous properties.
- Non-impervious clothing which becomes contaminated with solid hexachloroethane or liquids containing hexachloroethane should be removed promptly and not reworn until the hexachloroethane is removed from the clothing.

SANITATION

- Workers subject to skin contact with solid hexachloroethane or liquids containing hexachloroethane should wash with soap or mild detergent and water any areas of the body which may have contacted hexachloroethane at the end of each work day.
- Skin that becomes contaminated with solid hexachloroethane or liquids containing hexachloroethane should be promptly washed or showered with soap or mild detergent and water to remove any hexachloroethane.
- Employees who handle solid hexachloroethane or liquids containing hexachloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where solid hexachloroethane or liquids containing hexachloroethane are handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hexachloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of pyrotechnics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in lubricants in foundries for mold treatment; extreme-pressure lubricants; use in preparation of nitrocellulose esters camphor substitutes; use as a fumigant, insecticide, fungicide, and animal antihelmintics; use as a modifier in manufacture of synthetic rubber	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a chemical additive; use to reduce ignitability of combustibles, and as submarine paint to prevent corrosion; as an additive to fire extinguishers	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If hexachloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If hexachloroethane gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquids containing hexachloroethane soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of hexachloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention immediately.

- **Swallowing**

When hexachloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If hexachloroethane is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing hexachloroethane should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Hexachloroethane may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hexachloroethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR HEXACHLOROETHANE

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
10 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
300 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any pesticide respirator providing protection against pesticides. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Hexachloronaphthalene (Halowax 1014)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_2Cl_6$
- Synonyms: Halowax 1014
- Appearance and odor: Light yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Halowax 1014 is 0.2 milligram of Halowax 1014 per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Halowax 1014 can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Overexposure to Halowax 1014 may cause an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, yellow jaundice, and possibly death.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Halowax 1014.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Halowax 1014 at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Since this substance is a known liver toxin, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Halowax 1014 vapor and dust are toxic to the liver and the skin. Repeated exposure to an average concentration of 8.9 mg/m^3 of a mixture of penta- and Halowax 1014 produced jaundice and was fatal to rats; the liver showed marked fatty degeneration and centrolobular necrosis. At concentrations of mixed penta- and Halowax 1014 averaging 1 to 2 mg/m^3, there were human fatalities due to acute yellow atrophy of the liver. Such exposures produced jaundice associated with nausea, indigestion, and weight loss. The acute late stage progresses from restlessness to confusion, fever, and coma. Exposure of workers by inhalation of vapor or dust, or by skin absorption, has caused a severe acneform dermatitis termed chloracne, as well as serious liver injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 335
2. Boiling point (760 mm Hg): 343 to 388 C (650 to 730 F) (approximately)
3. Specific gravity (water = 1): 1.78
4. Vapor density (air = 1 at boiling point of Halowax 1014): 11.6
5. Melting point: 137 C (279 F)

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Halowax 1014 reacts with strong oxidizing agents.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when Halowax 1014 decomposes.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

No quantitative data are available on the relationship between air concentrations of the chloronaphthalenes and warning properties. Vapor pressure at 20 C is less than 1 mm Hg, creating a concentration of less than 1500 ppm at 20 C.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of Halowax 1014 on a filter, followed by extraction with hexane, and gas chromatographic analysis. An analytical method for Halowax is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten Halowax 1014.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid Halowax 1014 or with liquids containing Halowax 1014.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with Halowax 1014 fumes from the heated material.
- Non-impervious clothing which becomes contaminated with molten Halowax 1014 should be removed immediately and not reworn until the Halowax 1014 is removed from the clothing.
- Non-impervious clothing which becomes contaminated with solid Halowax 1014 or liquids containing Halowax 1014 should be removed promptly and not reworn until the Halowax 1014 is removed from the clothing.
- If employees' clothing may have become contaminated with solid Halowax 1014, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with Halowax 1014 should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of Halowax 1014 from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the Halowax 1014, the person performing the operation should be informed of Halowax 1014's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten Halowax 1014 contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where solid Halowax 1014 or liquids containing Halowax 1014 may contact the eyes.

SANITATION

- Eating and smoking should not be permitted in areas where Halowax 1014 is handled, processed, or stored.

- Workers subject to skin contact with Halowax 1014 should wash with soap or mild detergent and water any areas of the body which may have contacted Halowax 1014 at the end of each work day.
- Skin that becomes contaminated with solid Halowax 1014 or liquids containing Halowax 1014 should be promptly washed or showered with soap or mild detergent and water to remove any Halowax 1014.
- Employees who handle Halowax 1014 should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Halowax 1014 may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture (pouring, dipping, and peeling) of electric equipment as insulating material	Local exhaust ventilation; personal protective equipment; general dilution ventilation with intake and exhaust fans
Use as an inert component of resins or polymers for coating or impregnating textiles, wood, paper for flame- and water-proofing, and fungicidal and insecticidal properties	Process enclosure; local exhaust ventilation with intake and exhaust fans; general dilution ventilation
Use as an additive to special lubricants	General dilution ventilation
Use as an additive to cutting oils and special lubricants	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of electrical equipment when substance used as insulating material	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer manufacture as fillers; use during manufacture of special lubricants	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid Halowax 1014 or liquids containing Halowax 1014 get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. If molten Halowax 1014 gets into the eyes, immediately flush the eyes with large amounts of water to remove the heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If non-impervious clothing becomes soiled with Halowax 1014, remove and clean the clothing before wearing again. If non-impervious clothing becomes heavily contaminated, it should be destroyed. If solid Halowax 1014 or liquids containing Halowax 1014 get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If skin irritation persists after washing, get medical attention. If molten Halowax 1014 gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of Halowax 1014, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention immediately.

- **Swallowing**

When Halowax 1014 has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Halowax 1014 is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing Halowax 1014

should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Halowax 1014 may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hexachloronaphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR HALOWAX 1014

Condition	**Minimum Respiratory Protection* Required Above 0.2 mg/m³**
Particulate or Vapor Concentration	
2 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against pesticides. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Hexane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3(CH_2)_4CH_3$
- Synonyms: Hexyl hydride; normal hexane
- Appearance and odor: Colorless liquid with a mild, gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hexane is 500 parts of hexane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of hexane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 100 ppm (350 mg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 510 ppm (1,800 mg/m³) averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hexane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to hexane may cause lightheadedness, giddiness, nausea, and headache. It may also cause irritation of the eyes and nose. Greater exposure may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure to the liquid may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hexane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hexane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Hexane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hexane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although hexane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although hexane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: The aforementioned examinations should be performed on an annual basis.

- **Summary of toxicology**

Hexane vapor is a narcotic; it also is a mild upper respiratory irritant. Polyneuropathy has been reported to occur in Japanese workers exposed to hexane vapors. Effects appeared to be reversible. Concentrations of 30,000 ppm produced narcosis in mice within 30 to 60

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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minutes; convulsions and death occurred at 35,000 to 40,000 ppm; at 64,000 ppm respiratory arrest was produced in 2.5 to 4.5 minutes from the start of exposure. Concentrations up to 8000 ppm produced no anesthesia. In human subjects, 2000 ppm for 10 minutes produced no effects, but 5000 ppm resulted in dizziness and a sensation of giddiness. Other investigators reported slight nausea, headache, and irritation of the eyes and throat at 1400 to 1500 ppm. In industrial practice, mild narcotic symptoms such as dizziness have been observed when concentrations exceeded 1000 ppm, but not below 500 ppm. Chronic effects have rarely been reported. The liquid is a defatting agent, and prolonged exposure may cause irritation of the skin. Aspiration may cause a chemical pneumonia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 86
2. Boiling point (760 mm Hg): 68.9 C (156 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of hexane): 3.0
5. Melting point: −95 C (−139 F)
6. Vapor pressure at 20 C (68 F): 124 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.014
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving hexane.
4. Special precautions: Hexane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −21.7 C (−7 F) (closed cup)
2. Autoignition temperature: 225 C (437 F)
3. Flammable limits in air, % by volume: Lower: 1.1; Upper: 7.5
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Irritation Levels: The *Documentation of TLV's* notes that "Drinker, Yaglou, and Warren found slight nausea, headache, and eye and throat irritation at 1400 to 1500 ppm. Nelson found no irritation at 500 ppm in unacclimated subjects."
3. Evaluation of Warning Properties: Since hexane can be detected at a concentration approximately 3 times the permissible exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hexane. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of hexane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hexane may be used. An analytical method for hexane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid hexane.
- Any clothing which becomes wet with liquid hexane should be removed immediately and not reworn until the hexane is removed from the clothing.
- Clothing wet with liquid hexane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hexane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hexane, the person performing the operation should be informed of hexane's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid hexane may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to hexane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid hexane should be promptly washed or showered with soap or mild detergent and water to remove any hexane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hexane may occur and control methods which may be effective in each case:

Operation	Controls
Use as an extractant of agricultural products	Process enclosure; general dilution ventilation
Use in manufacture of polyolefins and certain elastomers as a catalyst carrier and assist in controlling molecular weight by dropping polymer out of solution when a certain molecular weight is reached	Process enclosure; general dilution ventilation; personal protective equipment
Use as an extractant of animal fat	Process enclosure; general dilution ventilation; personal protective equipment
Use as a solvent in adhesives to control viscosity and reduce drying time	General dilution ventilation; personal protective equipment
Use in pharmaceutical industry as a reaction medium, immiscible solvent, and extraction ergot	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during compounding of adhesives as a diluent or vehicle solvent; use in compounding printing inks, lacquers, or stains; use as a laboratory reagent and general solvent; use in manufacture of low-temperature thermometers	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If hexane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If hexane gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If hexane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of hexane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If hexane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If hexane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Hexane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Hexane may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR HEXANE

Condition	**Minimum Respiratory Protection* Required Above 500 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

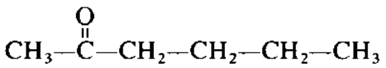
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-HEXANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-hexanone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{12}O$
- **Structure:**



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_2-CH_3$$

- **Synonyms:** Butyl methyl ketone, MBK, methyl butyl ketone, methyl n-butyl ketone
- **Identifiers:** CAS 591-78-6; RTECS MP1400000; DOT not assigned
- **Appearance and odor:** Colorless liquid with an odor like acetone but more pungent

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100.18
2. Boiling point (at 760 mmHg): 127.8°C (262°F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of 2-hexanone): 3.5
5. Melting point: -57°C (-71°F)
6. Vapor pressure at 20°C (68°F): 3.0 mmHg; at 25°C (77°F), 3.8 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.4
8. Evaporation rate (butyl acetate = 1): Approximately 1
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.4% (4,000 ppm); at 25°C (77°F), 0.5% (5,000 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving 2-hexanone.
3. Caution: 2-Hexanone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 25°C (77°F) (closed cup)
2. Autoignition temperature: 425°C (795°F)
3. Flammable limits in air, % by volume: Lower, 1.2; upper, 8
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 0.076 ppm
2. Eye irritation levels: 1,000 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-hexanone can be detected below the National Institute for Safety and Health (NIOSH) recommended exposure limit (REL); thus, 2-hexanone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-hexanone is 100 parts of 2-hexanone per million parts of air (ppm) [410 milligrams of 2-hexanone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 1 ppm (4 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (20 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for 2-hexanone

	Exposure limits	
	ppm	**mg/m^3**
OSHA PEL TWA	100	410
NIOSH REL TWA	1	4
ACGIH TLV® TWA	5	20

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Hexanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of 2-hexanone by guinea pigs caused central nervous system depression, narcosis, coma, and death. Subchronic inhalation of 2-hexanone by rats, cats, dogs, chickens, and monkeys produced peripheral neuropathy, characterized by paralysis, nerve swelling, and loss of nerve sheath covering.
2. *Effects on humans:* Chronic inhalation or dermal exposure of workers has caused peripheral neuropathy.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 2-hexanone can cause headaches, drowsiness, and unconsciousness. Moderate irritation of the eyes, nose, and throat can also occur.
2. *Long-term (chronic):* Exposure to 2-hexanone can cause lightheadedness, weight loss, fatigue, intermittent tingling or prickling sensations in the arms or legs, and progressive weakness of the limbs. Dryness, irritation, and inflammation of the skin can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 2-hexanone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-hexanone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or chronic concurrent dermatitis, or a history and physical findings consistent with peripheral neuropathy. In addition to the medical interview and physical examination, the means to identify these conditions may include electromyography of the extremities using standardized methods and evaluation criteria.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-hexanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and respiratory and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 2-hexanone may cause peripheral neuropathy after a prolonged period of induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Inflammatory and toxic neuropathy.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to 2-hexanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting 2-hexanone vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure 2-hexanone may also be used if available. A detailed sampling and analytical method for 2-hexanone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with 2-hexanone.

Workers should be provided with and required to use splash-proof safety goggles where 2-hexanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-hexanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-hexanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-hexanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with 2-hexanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-hexanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-hexanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 2-hexanone

Operations	Controls
During use as a commercial solvent for nitrocellulose, natural and synthetic resins, oils, waxes, vinyl polymers and copolymers, and cellulose acetates	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a solvent in the manufacture of varnish removers, vinyl lacquers, and nitrate wood lacquers	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as an extractive solvent for paraffin wax; during use in the separation and purification of certain metals	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-hexanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-hexanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-hexanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-hexanone gets on the skin, wash it immediately with soap and water. If 2-hexanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 2-hexanone is spilled or leaked, the following steps should be taken:
1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing 2-hexanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from 2-hexanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-hexanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Hexanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-hexanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for 2-hexanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 10 ppm	Any supplied-air respirator Any self-contained breathing apparatus
Less than or equal to 25 ppm	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 50 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode
Less than or equal to 1,000 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Less than or equal to 2,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 2,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (4 mg/m^3) (TWA).

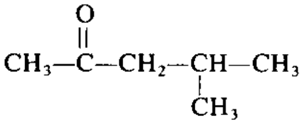
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HEXONE

INTRODUCTION

This guideline summarizes pertinent information about hexone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{12}O$
- **Structure:**



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

- **Synonyms:** Isobutyl methyl ketone; isopropylacetone; methyl isobutyl ketone; 4-methyl-2-pentanone; MIBK
- **Identifiers:** CAS 108-10-1; RTECS SA9275000; DOT 1245, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a sweet, pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100.18
2. Boiling point (at 760 mmHg): 118 °C (244°F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of hexone): 3.5
5. Melting point: -84°C (-119 °F)
6. Vapor pressure at 25 °C (77 °F): 7.5 mmHg
7. Solubility in water, g/100 g water at 20 °C (68 °F): 1.9
8. Evaporation rate (butyl acetate = 1): 1.64
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 1.0% (10,000 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving hexone.
3. Caution: Hexone will dissolve some plastics, resins, and rubber.

- **Flammability**

1. Flash point: 18 °C (64°F) (closed cup)
2. Autoignition temperature: 460 °C (860 °F)
3. Flammable limits in air, % by volume: Lower, 1.4; upper, 7.5
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 0.68 ppm
2. Eye irritation level: 200-400 ppm
3. Nose and throat irritation may occur at 400 ppm.
4. Evaluation of warning properties for respirator selection: Because of its odor, hexone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, hexone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hexone is 100 parts of hexone per million parts of air (ppm) [410 milligrams of hexone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (200 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (205 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek; and the ACGIH short-term exposure limit (STEL) is 75 ppm (300 mg/m^3) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for hexone

	Exposure limits ppm	Exposure limits mg/m³
OSHA PEL TWA	100	410
NIOSH REL TWA	50	200
ACGIH TLV® TWA	50	205
STEL	75	300

HEALTH HAZARD INFORMATION

• Routes of exposure

Hexone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Subchronic inhalation of hexone by rats produced degeneration and necrosis of kidney tubules and increased kidney and liver weights.

2. *Effects on humans:* Inhalation exposure of workers to hexone has produced narcosis and slight liver enlargement.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to hexone can cause nausea, vomiting, headaches, weakness, dizziness, incoordination, and drowsiness. Irritation of the eyes, nose, throat, and respiratory tract can also occur.

2. *Long-term (chronic):* Exposure to hexone can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to hexone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and reproductive, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to hexone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to hexone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to hexone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting hexone vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure hexone may also be used if available. A detailed sampling and analytical method for hexone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with hexone.

Workers should be provided with and required to use splash-proof safety goggles where hexone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with hexone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of hexone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hexone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with hexone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hexone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to hexone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for hexone

Operations	Controls
During application and drying of lacquers, varnishes, epoxy, acrylic, vinyl, or other cellulose- or resin-based coatings, finishes, and adhesives	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a separating agent for certain inorganic salts	General dilution ventilation
During extraction in the manufacture of antibiotics and purification of petroleum products (dewaxing)	General dilution ventilation
During the manufacture of dry cleaning preparations, germicides, fungicides, and electroplating solutions	General dilution ventilation
During use in blending raw materials for molded plastics	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in cleaning and maintaining ketone processing equipment	General dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to hexone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hexone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to hexone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hexone gets on the skin, wash it immediately with soap and water. If hexone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If hexone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing hexone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from hexone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing hexone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Hexone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing hexone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for hexone

Condition	Minimum Respiratory Protection*†
Concentration:	
Less than or equal to 500 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1,000 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 1,250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 2,500 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any supplied air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 3,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 3,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 50 ppm 200 mg/m^3) (TWA).

Occupational Health Guideline for sec-Hexyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$
- Synonyms: 1,3-Dimethylbutyl acetate; methylamyl acetate; methylisoamyl acetate; methylisobutyl carbinol acetate; hexyl acetate
- Appearance and odor: Colorless liquid with a mild, pleasant, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sec-hexyl acetate is 50 parts of sec-hexyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of sec-hexyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

sec-Hexyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- ***Effects of overexposure***

1. Short-term Exposure: Overexposure to sec-hexyl acetate may cause eye and throat irritation. It may also cause headache, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged exposure to sec-hexyl acetate may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sec-hexyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sec-hexyl acetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from sec-hexyl acetate exposure.

—Kidney disease: Although sec-hexyl acetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of sec-hexyl acetate might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although sec-hexyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: sec-Hexyl acetate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

High concentrations of sec-hexyl acetate vapor may be mildly irritating to the eyes and upper respiratory tract. The lethal dose for animals by inhalation is approximately 4000 ppm, although rats survived 8 hour exposures to concentrated vapors. This agent is poorly absorbed through the skin. No chronic systemic effects have been reported in humans.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 144
2. Boiling point (760 mm Hg): 141 C (285 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of sec-hexyl acetate): 5.0
5. Melting point: −64 C (−83 F)
6. Vapor pressure at 20 C (68 F): 4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.13
8. Evaporation rate (butyl acetate = 1): 0.47

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving sec-hexyl acetate.
4. Special precautions: None

- **Flammability**

1. Flash point: 45 C (113 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 0.9 (calculated at flash point)
4. Extinguishant: Dry chemical, foam, or carbon dioxide

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* reports that human subjects noted an unpleasant odor at 100 ppm.
2. Eye Irritation Level: The *Documentation of TLV's* also reports that eye irritation was experienced by human subjects exposed to 100 ppm. The TLV was recommended "to prevent significant eye irritation."
3. Other Information: According to the *Documentation of TLV's*, the human subject noted an unpleasant taste at 100 ppm.
4. Evaluation of Warning Properties: At a concentration of only twice the permissible exposure limit, human subjects can detect sec-hexyl acetate through odor, eye irritation, and taste. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of sec-hexyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sec-hexyl acetate may be used. An analytical method for sec-hexyl acetate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid sec-hexyl acetate.
- Clothing wet with liquid sec-hexyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sec-hexyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sec-hexyl acetate, the person performing the operation should be informed of sec-hexyl acetate's hazardous properties.
- Non-impervious clothing which becomes wet with sec-hexyl acetate should be removed promptly and not reworn until the sec-hexyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid sec-hexyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid sec-hexyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any sec-hexyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sec-hexyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use during application of nitrocellulose lacquers and other lacquers	General dilution ventilation; local exhaust ventilation
Liberation during manufacture of nitrocellulose and other lacquers	General dilution ventilation
Liberation during use as an inhibitor in handling of diacyl peroxide solutions	Process enclosure; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If sec-hexyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If sec-hexyl acetate gets on the skin, promptly flush the contaminated skin with water. If sec-hexyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of sec-hexyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When sec-hexyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If sec-hexyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Liquid sec-hexyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

sec-Hexyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR SEC-HEXYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
4000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HYDRAZINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about hydrazine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** N_2H_4
- **Structure:** $H_2N\text{-}NH_2$
- **Synonyms:** Diamide, diamine, hydrazine base, hydrazine anhydrous
- **Identifiers:** CAS 302-01-2; RTECS MU7175000; DOT 2029, label required: "Flammable Liquid and Poison"
- **Appearance and odor:** Colorless oily liquid that fumes in air and has a fishy or ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 32.06
2. Boiling point (at 760 mmHg): 113.5°C (236°F)
3. Specific gravity (water = 1): 1.004
4. Vapor density (air = 1 at boiling point of hydrazine): 1.04
5. Melting point: 1.4°C (34°F)
6. Vapor pressure at 25°C (77°F): 14.4 mmHg
7. Miscible with water
8. Evaporation rate (butyl acetate = 1): 0.42
9. Saturation concentration in air (approximate) at 25°C (77°F): 1.89% (18,900 ppm)
10. Ionization potential: 8.36 eV

- **Reactivity**

1. Incompatibilities: Hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving hydrazine.
3. Caution: Hydrazine will attack cork and some forms of plastic, coatings, and rubber.

- **Flammability**

1. Flash point: 37.7°C (100°F) (closed cup)
2. Autoignition temperature: 24°C (75.2°F) on iron rust surface, 270°C (518°F) on glass surface
3. Flammable limits in air, % by volume: Lower, 4.7; Upper, 98
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Caution: Hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

Odor threshold: 3-4 ppm

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hydrazine is 1.0 part of hydrazine per million parts of air (ppm) [1.3 milligrams of hydrazine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that hydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.03 ppm (0.04 mg/m^3) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the

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lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienist (ACGIH) has designated hydrazine as an A2 substance (suspected human carcinogen) having as assigned threshold limit value (TLV®) of 0.1 ppm (0.1 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for hydrazine

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	1.0	1.3
NIOSH REL (Ca)†		
Ceiling (120 min)	0.03	0.04
ACGIH TLV® (A2)§		
TWA (Skin)	0.1	0.1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute exposure of multiple species of animals to hydrazine by several routes of administration caused loss of appetite and weight, lethargy, vomiting, significant irritation of eyes, skin, and mucous membranes, hemolysis, fatty degeneration and lipid deposition in the liver and kidneys, and central nervous system (CNS) effects manifested by convulsions and death. Subchronic or chronic exposure of mice and rats to hydrazine by several routes of administration produced cancers of the liver, lung, or lymph tissues.
2. *Effects on humans:* A worker exposed to hydrazine hydrate once a week for six months developed fluid in the chest cavity, pulmonary edema, bronchitis, enlarged liver and kidneys, tissue destruction (necrosis) of the liver, intestinal hemorrhage, and death.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to hydrazine can cause dizziness, nausea, skin burns, and irritation of the eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to hydrazine can cause lethargy, vomiting, tremors, itching and burning of the eyes and skin, conjunctivitis, and contact dermatitis.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to hydrazine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and hematopoietic (blood-cell forming), nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to hydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to hydrazine.

- **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to hydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and hematopoietic, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to hydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**
Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of hydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**
Sampling and analysis may be performed by collecting hydrazine vapors with hydrochloric acid-filled midget bubblers and analyzing by visible absorption spectrophotometry. Direct-reading devices calibrated to measure hydrazine may also be used if available. A detailed sampling and analytical method for hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 3503).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with hydrazine.

SANITATION

Clothing which is contaminated with hydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with hydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to hydrazine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for hydrazine

Operations	Controls
During use in the synthesis and handling of high-energy fuels, agricultural chemicals, pharmaceuticals, chemicals for plastics and rubber manufacturing, textile agents and dye intermediates, and photographic chemicals	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an anticorrosion agent; during use in the application of metal coatings on nonconducting materials	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to hydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hydrazine gets on the skin, wash it immediately with soap and water. If hydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing hydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Hydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for hydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Hydrogen Bromide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HBr
- Synonyms: Anhydrous hydrobromic acid
- Appearance and odor: Colorless gas with an irritating, sharp odor. It also can be a liquid when stored under pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen bromide is 3 parts of hydrogen bromide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 10 milligrams of hydrogen bromide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen bromide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Hydrogen bromide may cause irritation of the eyes, nose, and throat. If a solution is splashed on the skin or in the eyes, it will cause a burn.

2. Long-term Exposure: Repeated or prolonged exposure to hydrogen bromide may cause irritation of the nose and throat with mucous production and indigestion.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen bromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen bromide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from hydrogen bromide exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hydrogen bromide might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Hydrogen bromide is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Hydrogen bromide is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Hydrogen bromide gas irritates the eyes, mucous membranes, and skin. Experimental exposure of humans to 5 ppm for several minutes caused nose and throat irritation in most individuals, and a few were affected at concentrations of 3 to 4 ppm. Solutions and the vapor irritate the upper respiratory tract. Contact with the eyes, skin, or mucous membranes may cause burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 80.92
  2. Boiling point (760 mm Hg): −66.8 C (−88.2 F)
  3. Specific gravity (water = 1): 2.16
  4. Vapor density (air = 1 at boiling point of hydro-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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gen bromide): 2.8

5. Melting point: −86.9 C (−124 F)

6. Vapor pressure at 16.8 C (62 F): 20 atm.

7. Solubility in water, g/100 g water at 20 C (68 F): 194

8. Evaporation rate (butyl acetate = 1): Not pertinent

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of liquid hydrogen bromide with strong oxidizers, strong caustics, metals, and moisture may cause violent spattering and fire.

3. Hazardous decomposition products: None

4. Special precautions: In the presence of moisture, hydrogen bromide liquid or gas will attack most metals with the formation of flammable hydrogen gas.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, the odor of hydrogen bromide is detectable at 2 ppm.

2. Eye Irritation Level: According to the *Documentation of TLV's*, no eye irritation was observed in human subjects exposed to concentrations up to 6 ppm. Kirk and Othmer state that hydrogen bromide is an eye irritant, but do not specify the necessary concentration.

3. Other Information: The *Documentation of TLV's* reports that 1 out of 6 human subjects experienced nose and throat irritation at 3 ppm hydrogen bromide. At 4 ppm, 3 out of 6 experienced nose irritation. All exposed subjects experienced nose irritation at 5 and 6 ppm. Only 1 out of 6 subjects experienced throat irritation at concentrations of 4 ppm, 5 ppm, and 6 ppm.

4. Evaluation of Warning Properties: Through its odor and irritant effects, hydrogen bromide can be detected at the permissible exposure limit or slightly above it. Therefore, hydrogen bromide is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of hydrogen bromide in a bubbler containing sodium hydroxide, followed by analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen bromide may be used. An analytical method for hydrogen bromide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid hydrogen bromide or solutions containing hydrogen bromide.
- Clothing contaminated with hydrogen bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen bromide, the person performing the operation should be informed of hydrogen bromide's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid hydrogen bromide or solutions containing hydrogen bromide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with hydrogen bromide should be removed immediately and not reworn until the hydrogen bromide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen bromide or solutions containing hydrogen bromide contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquid hydrogen bromide or solutions containing hydrogen bromide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with hydrogen bromide should be immediately washed or showered to remove any hydrogen bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of inorganic bromides for use in photography, pharmaceuticals, industrial drying, textile finishing, engraving and lithography, chemical synthesis, and fire retardants	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of brominated fluorocarbons for fire extinguishing, refrigeration, and aerosols	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis as intermediates for barbituate manufacture, manufacture of synthetic hormones, catalyst for alkylations, controlled oxidations, isomerizations, and polymerizations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during decomposition of brominated fluorocarbon fire-extinguishing agents or flame-retardant chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a reagent in analytical chemistry; use in etching of germanium crystals, silicon discs, and metal alloys	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for ore minerals	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid hydrogen bromide or solutions containing hydrogen bromide get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid hydrogen bromide or solutions containing hydrogen bromide get on the skin, immediately flush the contaminated skin with water. If liquid hydrogen bromide or solutions containing hydrogen bromide penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of hydrogen bromide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If a solution of hydrogen bromide has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the hydrogen bromide. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If hydrogen bromide is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the

open air, and repair the leak or allow the cylinder to empty.

3. If in the liquid form, allow to vaporize and disperse the gas.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hydrogen Bromide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Bromine," *Hygienic Guide Series*, Detroit, Michigan, 1958.
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RESPIRATORY PROTECTION FOR HYDROGEN BROMIDE

Condition	**Minimum Respiratory Protection* Required Above 3 ppm**
Gas or Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with a full facepiece and an acid gas cartridge(s). A gas mask with a chin-style or a front- or back-mounted acid gas canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 50 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Hydrogen Chloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HCl
- Synonyms: Anhydrous hydrogen chloride; hydrochloric acid, anhydrous
- Appearance and odor: Colorless gas with an irritating, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen chloride is a ceiling of 5 parts of hydrogen chloride per million parts of air (ppm). This may also be expressed as 7 milligrams of hydrogen chloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen chloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: When hydrogen chloride gas is inhaled, it may cause irritation of the respiratory tract with burning, choking, and coughing. Severe breathing difficulties may occur which may be delayed in onset. At times ulceration of the nose and throat may occur. Hydrogen chloride gas and solutions of hydrogen chloride (hydrochloric acid) may cause eye irritation, severe burns, and permanent damage with loss of sight. Solutions of hydrogen chloride may cause severe burns of the skin unless the acid is washed off immediately. Exposure of the skin to hydrogen chloride gas may cause skin inflammation or burns. Swallowing hydrogen chloride solution may cause burns of the mouth, throat, and stomach.

2. Long-term Exposure: Repeated or prolonged exposure to hydrogen chloride may cause erosion of the teeth. Repeated exposure of the skin to dilute solutions of hydrogen chloride may cause skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen chloride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, skin, and eyes should be stressed.

—14" x 17" chest roentgenogram: Hydrogen chloride causes lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen chloride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Hydrogen chloride gas irritates the eyes, mucous membranes, and skin. Exposure of rabbits and guinea pigs to 6400 mg/m^3 (approximately 4290 ppm) for 30 minutes caused death, in many instances from laryngeal spasm, laryngeal edema, or pulmonary edema. Exposure of three species of animals to 300 ppm for 6 hours caused

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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corneal and upper respiratory irritation. In humans, exposure to the gas immediately causes severe irritation of the upper respiratory tract resulting in cough, burning of the throat, and a choking sensation; effects are usually limited to inflammation and occasionally ulceration of the nose, throat, and larynx; if inhaled deeply, pulmonary edema may occur. In workers, exposure to 50 to 100 ppm for 1 hour was barely tolerable; short exposure to 35 ppm caused irritation of the throat, and 10 ppm was considered the maximal concentration allowable for prolonged exposure. High concentrations of the gas caused eye irritation and may cause prolonged or permanent visual impairment, including total loss of vision. Exposure of the skin to a high concentration of the gas or to a concentrated solution of the gas (hydrochloric acid) will cause burns; repeated or prolonged exposure to dilute solutions may cause dermatitis. Erosion of the teeth may occur from repeated or prolonged exposure. Although unlikely to occur, ingestion of hydrochloric acid causes severe burns of the mucous membranes of the mouth, esophagus, and stomach; pain; nausea and vomiting.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 36.5
2. Boiling point (760 mm Hg): −85 C (−121 F)
3. Specific gravity (water = 1): 1.194 (liquid)
4. Vapor density (air = 1 at boiling point of hydrogen chloride): 1.27
5. Melting point: −114 C (−173 F) (triple point)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 62
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause cylinders to burst.
2. Incompatibilities: Contact with most metals corrodes them severely and forms flammable hydrogen gas. Contact of hydrogen chloride gas or liquid with any alkali or active metal may develop enough heat to cause fire in adjacent combustible material.
3. Hazardous decomposition products: None
4. Special precautions: Hydrogen chloride will attack most metals and some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Patty notes that according to Hirt, a concentration of 35 ppm "cannot be detected by taste or odor. (Editor's note: Most people can detect 1 to 5 ppm; 5 to 10 ppm is disagreeable)." The editor does not specify how most people can detect 1 to 5 ppm, however.
2. Eye Irritation Level: Grant states that an exposure of animals to "100 ppm for 6 hours daily for 50 days caused only slight unrest and irritation of the eyes, but no injury."
3. Other Information: The *Documentation of TLV's* states that hydrogen chloride is a strong irritant. Thirty-five ppm "caused irritation of the throat on short exposure . . . . Elkins states, however, that hydrogen chloride was immediately irritating when inhaled at concentrations of 5 ppm or more."
4. Evaluation of Warning Properties: Through its irritant effects, hydrogen chloride can be detected at or slightly above the permissible exposure limit. For the purposes of this guideline, therefore, hydrogen chloride is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen chloride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of hydrogen chloride in a bubbler containing sodium acetate solution, followed by dilution with water, and analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen chloride may be used. An analytical method for hydrogen chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted

are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with mists or solutions of hydrogen chloride which have a pH less than 3.0.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with mists or solutions of hydrogen chloride which have a pH equal to or greater than 3.0.
- Where there is any possibility of exposure of an employee's body to solutions of hydrogen chloride which have a pH less than 3.0, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with solutions of hydrogen chloride which have a pH less than 3.0 should be removed immediately and not reworn until the hydrogen chloride is removed from the clothing.
- Non-impervious clothing which becomes wet with solutions of hydrogen chloride with a pH equal to or greater than 3.0 should be removed promptly and not reworn until the hydrogen chloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of mists of solutions of hydrogen chloride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solutions of hydrogen chloride which have a pH less than 3.0, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with solutions of hydrogen chloride which have a pH less than 3.0 should be immediately washed or showered to remove any hydrogen chloride.
- Skin that becomes wet with solutions of hydrogen chloride which have a pH equal to or greater than 3.0 should be promptly washed or showered to remove any hydrogen chloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use during pickling of metals including stainless steel, iron, nickel, and monel	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use as a catalyst or chlorinating agent in chemical synthesis; use during metal treatment and fabricating operations in electroplating, acid dipping, stripping, electropolishing, etching, welding, and flame-cutting of metal primed with paint or cleaned with chlorinated hydrocarbons, and used as a gaseous flux in babbitting	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in oxyhydrochlorination processing in production of chlorinated hydrocarbons	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in food processing and manufacture including sugar cane refining, glucose, and corn sugar, and brewing operations	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in industrial chemical cleaning operations; use in production of plastics and resins	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in rubber manufacture including synthesis of chloroprene; use as a chlorinating agent and in coagulation of latex	Local exhaust ventilation; general mechanical ventilation; personal protective equipment

Operation	Controls
Liberation during synthesis of other organic chemicals; use in extraction and reduction processing of metal ores	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use as a deliner of hides in leather manufacture	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in activation of petroleum wells; use in waste treatment operations for neutralization of alkaline waste streams; use in production of chlorine	Local exhaust ventilation; general mechanical ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solutions of hydrogen chloride or strong concentrations of hydrogen chloride gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solutions of hydrogen chloride or strong concentrations of hydrogen chloride gas get on the skin, immediately flush the contaminated skin with water. If solutions of hydrogen chloride or strong concentrations of hydrogen chloride gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of hydrogen chloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If solutions of hydrogen chloride have been swallowed and the person is conscious, give him large amounts of water to dilute the hydrogen chloride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If hydrogen chloride gas is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

- If solutions of hydrogen chloride are spilled, the following steps should be taken:

1. Collect or confine spilled material in the most convenient and safe manner.
2. If possible, reclaim the spilled material. If this is not possible;
3. dilute and/or neutralize and dispose in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hydrogen Chloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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phia, 1958.

RESPIRATORY PROTECTION FOR HYDROGEN CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
50 ppm or less	Any chemical cartridge respirator with an acid gas cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	Any chemical cartridge respirator with a full facepiece and an acid gas cartridge(s). A gas mask with a chin-style or a front- or back-mounted acid gas canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen chloride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Cyanide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HCN
- Synonyms: Hydrocyanic acid; prussic acid; formonitrile
- Appearance and odor: Colorless or pale blue liquid or gas with a bitter almond odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen cyanide is 10 parts of hydrogen cyanide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 11 milligrams of hydrogen cyanide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 5 mg cyanide/m^3 averaged over a 10-minute period. The NIOSH Criteria Document for Hydrogen Cyanide and Cyanide Salts should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen cyanide can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Inhalation, ingestion, or skin absorption of hydrogen cyanide may be rapidly fatal. Larger doses may cause the person to rapidly lose consciousness, stop breathing, and die. At lower levels of exposure, a person may experience weakness, headache, confusion, nausea, and vomiting. These symptoms may be followed by unconsciousness and death. Hydrogen cyanide liquid may irritate the eyes.
2. *Long-term Exposure:* Effects from chronic exposure to hydrogen cyanide are non-specific and rare.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen cyanide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen cyanide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of fainting spells, such as occur in various types of cardiovascular and nervous disorders, and and those who are unusually susceptible to effects of anoxia or with anemia would be expected to be at increased risk from exposure. Examination of the cardiovascular, nervous, and upper respiratory systems, and thyroid should be stressed.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.
3. *First Aid Kits:* First aid kits should be immediately available in workplaces where there is a potential for the release of hydrogen cyanide. These kits should contain a minimum of 48 ampules, each of 0.3 ml amyl nitrate, and complete instructions for use. In addition, 2 physician's kits should be immediately available to trained medical personnel. These kits should contain the above quantity of amyl nitrate as well as sterile sodium

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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nitrite solution (3%) and sterile sodium thiosulfate solution (25%). All of the above drugs should be replaced at least biannually to ensure their potency.

- **Summary of toxicology**

Hydrogen cyanide (HCN) vapor, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. Cyanide exerts this effect because it inactivates certain enzymes by forming very stable complexes with the metal in them. Cytochrome oxidase is probably the most important of these since it occupies a fundamental position in the respiratory process and is involved in the ultimate electron transfer to molecular oxygen. Since cytochrome oxidase is present in practically all cells that function under aerobic conditions, and since the cyanide ion diffuses easily to all parts of the body, it is capable of suddenly bringing to a halt practically all cellular respiration. A few inhalations of high concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, 135 ppm after 30 minutes, and 110 ppm may be fatal in 1 hour. At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth usually increase initially and at later stages become slow and gasping; if cyanosis is present, it usually indicates that respiration has either ceased or has been very inadequate for a few minutes. Humans tolerate 45 to 54 ppm for ½ to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours. The ingestion by humans of 50 to 100 mg of HCN may also be fatal. Eye contact with liquid HCN may cause irritation. Cyanide is one of the few toxic substances for which an antidote exists, and it functions as follows. First, amyl nitrite (inhalation) and sodium nitrite (intravenously) are administered to form methemoglobin, which binds firmly with free cyanide ions. This traps any circulating cyanide ions. The formation of 10 to 20% methemoglobin usually does not involve appreciable risk, yet provides a large amount of cyanide-binding substance. Second, sodium thiosulfate is administered intravenously to increase the rate of conversion of cyanide to the less toxic thiocyanate. Methylene blue should not be administered, because it is a poor methemoglobin former and, moreover, promotes the conversion of methemoglobin back to hemoglobin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 27
2. Boiling point (760 mm Hg): 26 C (79 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of hydrogen cyanide): 0.93
5. Melting point: −14.4 to −16.8 C (7 to 2 F)
6. Vapor pressure at 20 C (68 F): 620 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Older samples may polymerize and explode unless acid stabilizer is maintained at proper concentration. Samples containing more than 2 − 5% of water are less stable than dry material. Samples stored more than 90 days are hazardous.
2. Incompatibilities: Contact with bases such as caustics and amines may cause violent polymerization and explosion.
3. Hazardous decomposition products: None more toxic than hydrogen cyanide.
4. Special precautions: Liquid hydrogen cyanide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −17.8 C (0 F) (closed cup)
2. Autoignition temperature: 538 C (1000 F)
3. Flammable limits in air, % by volume: Lower: 5.6; Upper: 40
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of HCN is usually described as 'sweet'; trained persons describe the odor as that of bitter almonds and can detect it at about one ppm." The Manufacturing Chemists Association (MCA) states that "although hydrocyanic acid has a characteristic odor, its toxic action at hazardous concentrations is so rapid that it is of no value as a warning."
2. Eye Irritation Level: Grant states that "only occasionally has reference been made to an irritation of the eye, conjunctivitis, or superficial keratitis developing after chronic exposure to hydrogen cyanide gas."
3. Evaluation of Warning Properties: For the purposes of this guideline, hydrogen cyanide has been treated as a material with poor warning properties. Although the odor threshold appears to be below the permissible exposure limit, Patty states that "the sense of smell is . . . easily fatigued; and there is wide individual variation in the minimum odor threshold."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen cyanide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Hydrogen cyanide may be monitored by collection in midget impingers containing sodium hydroxide, followed by analysis with an ion specific electrode. An analytical method for hydrogen cyanide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid hydrogen cyanide.
- Where there is any possibility of exposure of an employee's body to liquid hydrogen cyanide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with, or non-impervious clothing which becomes contaminated with, liquid hydrogen cyanide should be removed immediately and not reworn until the hydrogen cyanide is removed from the clothing.
- Clothing wet with hydrogen cyanide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen cyanide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen cyanide, the person performing the operation should be informed of hydrogen cyanide's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen cyanide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to hydrogen cyanide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with hydrogen cyanide should be immediately washed or showered to remove any hydrogen cyanide.
- Employees who handle hydrogen cyanide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen cyanide may occur and control methods which may be effective in each case:

Operation	Controls
Use in fumigation of structures and agricultural crops	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use of cyanide salts or solutions in metal treatment operations, blast furnace and coke oven operations, metal ore processing, and photoengraving operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of intermediates in synthesis of acrylic plastics, nylon 66, chelating agents, dyes, pharmaceuticals, and specialty chemicals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid hydrogen cyanide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid hydrogen cyanide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen cyanide soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of hydrogen cyanide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When hydrogen cyanide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If hydrogen cyanide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Hydrogen cyanide should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of hydrogen cyanide vapors are permitted.

- Waste disposal method:

Liquid hydrogen cyanide may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR HYDROGEN CYANIDE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen cyanide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen cyanide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 50 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Fluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HF
- Synonyms: Anhydrous hydrofluoric acid; HF-A
- Appearance and odor: Colorless, fuming liquid or gas with a strong irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen fluoride is 3 parts of hydrogen fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2 milligrams of hydrogen fluoride per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 2.5 mg fluoride/m^3 averaged over a work shift of not more than 10 hours per day, 40 hours per week, with a ceiling level of 5 mg fluoride/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Hydrogen Fluoride should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen fluoride can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Hydrogen fluoride liquid or vapor causes severe irritation and deep-seated burns of the eye and eye lids if it comes in contact with the eyes. If the chemical is not removed immediately, permanent visual defects or blindness may result. When lower concentrations (20% or less) come into contact with the skin, the resulting burns do not usually become apparent for several hours. Skin contact with higher concentrations is usually apparent in a much shorter period, if not immediately. The skin burns may be very severe and painful. Hydrofluoric acid is a severe irritant to the nose, throat, and lungs. Severe exposure causes rapid inflammation and congestion of the lungs. Breathing difficulties may not occur until some hours after exposure has ceased. Death may occur from breathing this chemical. If swallowed, hydrofluoric acid will immediately cause severe damage to the throat and stomach.

2. Long-term Exposure: Prolonged or repeated exposure to lower concentrations of hydrogen fluoride vapor may cause changes in the bones. Exposure to low concentrations of vapors of hydrogen fluoride may also cause chronic irritation and congestion of the nose, throat, and bronchial tubes.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen fluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, central nervous system, skeletal system, and the kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in acute overexposures to hydrogen fluoride, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centri-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

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Occupational Safety and Health Administration

fuged sediment. An analysis for fluoride should be performed.

—Pelvic roentgenogram: Hydrogen fluoride may cause skeletal abnormalities. A radiologic examination of the male pelvis with proper gonadal shielding should be conducted at the time of the preplacement examination and when indicated by analysis of the results of the urinary hydrogen fluoride tests.

—Eye disease: Hydrogen fluoride is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Hydrogen fluoride may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen fluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Hydrogen fluoride can cause dermatitis on prolong exposure to concentrations from 1.8 to 8.1 mg/m^3. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that the radiologic examination of the pelvis should be conducted only when clinically indicated.

- **Summary of toxicology**

Hydrogen fluoride as a gas is a severe respiratory irritant, and in solution causes severe and painful burns of the skin. Animals repeatedly exposed to 17 ppm showed damage to the lungs, liver, and kidneys, but at 8.6 ppm there was only occasional lung injury. Fatalities occurred in 3 of 6 workers exposed to spills of 70% solutions on the skin and inhalation of the vapor; despite prompt showering with water for skin burns, death from pulmonary edema occurred 2 hours after exposure. A chemist, splashed on the face and upper extremities with hydrogen fluoride, developed pulmonary edema 3 hours after exposure and died 10 hours later. In human subjects, 120 ppm was the highest concentration that could be tolerated for 1 minute, because of the onset of conjunctival and respiratory irritation with stinging of the skin. Repeated experimental human exposures to concentrations of 2 ppm for 6 hours daily caused a slight stinging of the eyes and skin of the face, with nasal irritation. Repeated exposures to low concentrations at work may produce chronic irritation of the nose, throat, and bronchi. Hydrogen fluoride solutions in contact with skin, if untreated, result in marked tissue destruction; the fluoride ion readily penetrates skin and deep tissue, causing necrosis of soft tissues and decalcification of bone. When skin contact is with solutions of less than 50% hydrogen fluoride, the burns do not become manifest immediately; burns from solutions stronger than 50% and anhydrous HF are felt in a matter of minutes, and because fluoride ions penetrate the skin readily, necrosis of deep tissue and damage to the bone may occur. Severe eye injuries from splashes may occur. In one case of eye burns from a fine spray of hydrofluoric acid in the face, considerable loss of corneal epithelium occurred despite immediate and copious flushing with water and irrigation for 3 hours with a 0.5% solution of benzethonium chloride; within 19 days there was recovery of normal vision.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 20
2. Boiling point (760 mm Hg): 19.5 C (67.1 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of hydrogen fluoride): 0.7
5. Melting point: −83.4 C (−118 F)
6. Vapor pressure at 20 C (68 F): 760 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of hydrogen fluoride (liquid or gas) with metals, concrete, glass, and ceramics causes severe corrosion. Contact with metals may form flammable hydrogen gas.
3. Hazardous decomposition products: None
4. Special precautions: Liquid or gaseous hydrogen fluoride will attack some forms of plastics, rubber, and coatings. It will also attack glass and other ceramic materials.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The Manufacturing Chemists Association reports that the vapor has a sharp and penetrating odor, but no quantitative information is available concerning the odor threshold.
2. Eye Irritation Level: Grant states that "air containing as little as 5 ppm (hydrogen fluoride) causes irritation of the eyes."
3. Other Information: According to Grant, irritation of the nose occurs at a concentration as low as 5 ppm.
4. Evaluation of Warning Properties: Since hydrogen fluoride can be detected through its irritant effects at a concentration slightly above the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen fluoride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of hydrogen fluoride in a bubbler, followed by dilution with a buffer, and analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen fluoride may be used. An analytical method for hydrogen fluoride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid hydrogen fluoride or solutions containing hydrogen fluoride.
- Clothing contaminated with hydrogen fluoride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen fluoride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen fluoride, the person performing the operation should be informed of hydrogen fluoride's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid hydrogen fluoride or solutions containing hydrogen fluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with hydrogen fluoride should be removed immediately and not reworn until the hydrogen fluoride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen fluoride or solutions containing hydrogen fluoride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid hydrogen fluoride or solutions containing hydrogen fluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.
- Whenever hydrogen fluoride is accidentally released into the workplace air, employees should be required to immediately evacuate the area.

SANITATION

- Skin that becomes contaminated with hydrogen fluoride should be immediately washed or showered to remove any hydrogen fluoride.
- Eating and smoking should not be permitted in areas where liquid hydrogen fluoride or solutions containing hydrogen fluoride are handled, processed, or stored.
- Employees who handle liquid hydrogen fluoride or solutions containing hydrogen fluoride should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen fluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of chlorofluorohydrocarbons for application as refrigerant fluids, aerosol propellants, specialty solvents, high-performance plastics, and foaming agents	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in cleaning sandstone and marble; use as a pickling agent for stainless steel and other metals; use as a cleaner in meat packing industry	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in manufacture of aluminum fluoride and synthetic cryolite for reduction of aluminum oxide to aluminum	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in electroplating operations	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from fertilizer manufacture	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid as a catalyst in alkylation of petroleum fractions to produce high-octane fuels	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in etching, frosting, and polishing glassware and ceramics	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an acidizing agent during injection of acid into oil wells	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in removal of sand and scale from foundry castings	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in separation and purification of uranium isotopes	Process enclsoure; local exhaust ventilation; personal protective equipment
Use in manufacture of insecticides; use of aqueous acid in treating textiles to remove trace metals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in production of fluorosilicone products	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in preparation of microelectronic circuits and quartz crystals for radio oscillators	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in manufacture of laundry sours and stain removers	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in extraction and purification of minerals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in manufacture of pharmaceuticals and special dyes	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid hydrogen fluoride or solutions containing hydrogen fluoride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid hydrogen fluoride or solutions containing hydrogen fluoride get on the skin, immediately flush the contaminated skin with water for a considerable time. If liquid hydrogen fluoride or solutions containing hydrogen fluoride penetrate through the clothing, remove the clothing immediately and flush the skin with water for a considerable time. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of hydrogen fluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid hydrogen fluoride or solutions containing hydrogen fluoride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the hydrogen fluoride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If hydrogen fluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in the liquid form, allow to vaporize and disperse the gas.

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RESPIRATORY PROTECTION FOR HYDROGEN FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Gas or Vapor Concentration	
20 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against hydrogen fluoride. A gas mask with a chin-style or a front- or back-mounted canister and filter providing protection against hydrogen fluoride. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 20 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen fluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen fluoride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Peroxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H_2O_2
- Synonyms: High-strength hydrogen peroxide; peroxide; hydrogen dioxide
- Appearance and odor: Colorless liquid with a slightly sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen peroxide is 1 part of hydrogen peroxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1.4 milligrams of hydrogen peroxide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen peroxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to vapor from hydrogen peroxide may cause extreme irritation of the eyes, nose, and throat. Splashes of hydrogen peroxide in the eyes may cause severe damage and possible blindness. Eye damage may appear a week or more after exposure. If the liquid is splashed on the skin, it may cause tingling and temporary whitening. If the skin is washed promptly, the skin will return to normal in 2 or 3 hours. If the hydrogen peroxide is not removed, redness and blister formation may result. If swallowed, hydrogen peroxide may cause injury to the mouth and throat with possible bleeding from the esophagus and stomach. The swallowed hydrogen peroxide may produce large quantities of oxygen gas which may distend the esophagus and stomach and cause severe damage.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen peroxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen peroxide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from hydrogen peroxide exposure.

—Eye disease: Hydrogen peroxide, 90 percent, is an eye irritant. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Hydrogen peroxide, 90 percent, causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hydrogen peroxide, 90 percent, might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Hydrogen peroxide, 90 percent, is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ninety percent hydrogen peroxide vapor, mist, or liquid irritates the eyes, mucous membranes, and skin. Repeated exposure of dogs to 7 ppm for 6 months caused sneezing, lacrimation, and bleaching of hair; at autopsy there was local atelectasis. In humans, inhalation of high concentrations of vapor or mist may cause extreme irritation and inflammation of the nose and

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throat. Exposure for a short period to mist or diffused spray may cause stinging of the eyes and lacrimation. Splashes of the liquid in the eyes may cause severe damage, including ulceration of the cornea; there may be a delayed appearance of damage to the eyes, and corneal ulceration has, on rare occasions, appeared even a week or more after exposure. Skin contact with the liquid for a short time will cause a temporary whitening or bleaching of the skin; if splashes on the skin are not removed, erythema and formation of vesicles may occur. Ingestion may cause irritation of the upper gastrointestinal tract; decomposition of the hydrogen peroxide will result in the rapid liberation of oxygen, which may distend and damage the esophagus or stomach.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 34
2. Boiling point (760 mm Hg): 141 C (286 F) (calculated)
3. Specific gravity (water = 1): 1.38
4. Vapor density (air = 1 at boiling point of hydrogen peroxide): Not applicable (decomposes)
5. Melting point: −11 C (12 F)
6. Vapor pressure at 30 C (86 F): 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Hydrogen peroxide decomposes slowly at ordinary temperatures and builds up pressure if the container is closed. The rate of decomposition doubles for each 10 C rise (1.5 times 10 C rise) in temperature and becomes self-sustaining at 141 C (285 F). Contaminated hydrogen peroxide can decompose at a rate that will exceed the capacity of the vent in the container. Hydrogen peroxide in concentrations up to about 90% does not readily detonate. Higher concentrations or elevated temperatures may facilitate detonation.
2. Incompatibilities: Contact with most organic or readily oxidizable materials and combustibles causes fires and explosions. Contact with iron, copper, brass, bronze, chromium, zinc, lead, manganese, silver, and other catalytic metals (or their salts) causes rapid decomposition with evolution of oxygen gas and heat which may increase container pressure.
3. Hazardous decomposition products: None
4. Special precautions: Liquid hydrogen peroxide will attack some forms of plastics, rubber, and coatings; many will ignite. The adiabatic decomposition temperature is 740 C (1364 F), so that most combustible materials in contact with the decomposition products will readily burst into flames.

- **Flammability**

1. Not combustible, but a powerful oxidizing agent

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of hydrogen peroxide.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the eyes do not appear to be damaged from exposure to the vapor." Grant reports, "Injuries of human eyes have been rare. Workers exposed to vapors from 90% hydrogen peroxide have noted primarily respiratory irritation, but a splash of such high concentration is generally feared as a potential cause of severe corneal damage....

'Experimental exposure of dogs to 7 ppm hydrogen peroxide in air 6 hours a day caused no adverse effect during 23 weeks but then began to cause sneezing and lacrimation. Rabbits similarly exposed for 10 weeks suffered no corneal damage."

Deichmann and Gerarde, however, note that "vapors are irritating to the eyes, nose and throat."

According to the *Hygienic Guide*, hydrogen peroxide can be "recognized only by irritant effects, especially in nasal passages." They give an irritation threshold of approximately 100 ppm.

3. Evaluation of Warning Properties: Hydrogen peroxide has poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for hydrogen peroxide had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforce-

ment and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid hydrogen peroxide.
- Clothing contaminated with hydrogen peroxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen peroxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen peroxide, the person performing the operation should be informed of hydrogen peroxide's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid hydrogen peroxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with hydrogen peroxide should be removed immediately and not reworn until the hydrogen peroxide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen peroxide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid hydrogen peroxide, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with hydrogen peroxide should be promptly washed or showered to remove any hydrogen peroxide.
- Employees who handle liquid hydrogen peroxide should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen peroxide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of propellants for military and space programs; use as a component of explosives	Process enclosure; general dilution ventilation; personal protective equipment; vented containers; ample available water supply
Use in chemical synthesis as an oxidant in organic and inorganic synthesis	Process enclosure; general dilution ventilation; personal protective equipment vented containers; ample available water supply
Use as a polymerization promoter; use as a bleaching agent for oils, waxes, fats, and discolored concentrated acids	Process enclosure; general dilution ventilation; personal protective equipment vented containers; ample available water supply

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid hydrogen peroxide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid hydrogen peroxide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen peroxide soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of hydrogen peroxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When hydrogen peroxide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If hydrogen peroxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Dilute with copious quantities of water.

- Waste disposal method:

After dilution with copious quantities of water, hydrogen peroxide may be flushed into a sewer.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hydrogen Peroxide (90%)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Hydrogen Peroxide (90%)," *Hygienic Guide Series*, Detroit, Michigan, 1957.
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RESPIRATORY PROTECTION FOR HYDROGEN PEROXIDE (90%)

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
10 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
75 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 75 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against hydrogen peroxide. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen peroxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 75 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Selenide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H_2Se
- Synonyms: Selenium hydride
- Appearance and odor: Colorless gas with a very offensive odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen selenide is 0.05 part of hydrogen selenide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of hydrogen selenide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen selenide can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to hydrogen selenide may cause irritation of the eyes, nose, throat, and lungs, nausea, vomiting, and diarrhea. Subsequently, there may be a metallic taste in the mouth, garlic odor of the breath, dizziness, and extreme tiredness. Hydrogen selenide has been known to cause pneumonia and liver damage in animals.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen selenide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen selenide at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from hydrogen selenide exposure.

—Chronic respiratory disease: Hydrogen selenide causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hydrogen selenide might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Hydrogen selenide causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Hydrogen selenide gas irritates the eyes, nose, and throat and causes pulmonary irritation in animals. Guinea pigs exposed to 10 ppm for 2 hours exhibited immediate irritation of the eyes and nose; a high percentage of the animals died, apparently from pneumonitis. Exposure of guinea pigs to 1 mg/m^3 (0.3 ppm) for 8 hours produced death in half of the animals; pulmonary irritation and liver damage were observed. In humans, a concentration of 1.5 ppm is said to produce intolerable irritation of the eyes and nose. Five workers exposed to concentrations of less than 0.2 ppm of hydrogen selenide and possibly other selenium compounds for 1 month developed nausea, vomiting, diarrhea, metallic taste in the mouth, garlic odor of the breath, dizziness, lassitude, and fatigability; following cessation of exposure, there was a gradual regression of symptoms during the succeeding months. Urinary selenium levels of the workers

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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ranged from 0 to 13.1 mg Se/100 cc urine; there was no correlation between symptoms and levels of urinary excretion.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 81
2. Boiling point (760 mm Hg): −41.3 C (−42 F)
3. Specific gravity (water = 1): Liquid = 2.1 at boiling point
4. Vapor density (air = 1 at boiling point of hydrogen selenide): 2.8
5. Melting point: −65.7 C (−86.5 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.73
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with oxidizers, acids, water, and halogenated hydrocarbons may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as selenium dioxide fume) may be released in a fire involving hydrogen selenide.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Shut off flow of gas; carbon dioxide

- **Warning properties**

1. Odor Threshold: May and Summer report odor thresholds for hydrogen selenide of 0.3 ppm and 3 ppm, respectively.
2. Irritation Level: Grant states that "a concentration of 1.5 ppm in air is said to produce intolerable irritation of the eyes and nose which tends to limit exposure and safeguard against injury. However, below 1 ppm the ocular and respiratory warning properties are insufficient to prevent exposure which may cause systemic intoxication." Dudley and Miller state that at 0.001 mg/l (0.3 ppm) "no eye or nasal irritation is produced in man."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of hydrogen selenide are not within three times the permissible exposure limit, hydrogen selenide is treated as a material with poor warning properties. In addition, the AIHA *Hygienic Guide* states that "the odor perception of it (hydrogen selenide) is soon lost."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for hydrogen selenide had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen selenide may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of semi-conductor materials; use in chemical synthesis for metal selenides and organoselenium, lasers, and emulsions	Process enclosure; local exhaust ventilation; personal protective equipment

Liberation from roasting of metal ores and pyrites, production of glass and ceramics, vulcanization of rubber, and etching with inks	Local exhaust ventilation; personal protective equipment
Liberation from overloaded selenium rectifiers	Local exhaust ventilation; personal protective equipment
Liberation from bacterial action of selenium-contaminated clothing	Good personal hygiene practice

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of hydrogen selenide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If hydrogen selenide is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak to disperse gas.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

- Waste disposal method:

Hydrogen selenide may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hydrogen Selenide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR HYDROGEN SELENIDE

Condition	**Minimum Respiratory Protection*** **Required Above 0.05 ppm**
Gas Concentration	
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen selenide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Hydrogen Sulfide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H_2S
- Synonyms: Sulfuretted hydrogen; hydrosulfuric acid; hepatic gas
- Appearance and odor: Colorless gas with a strong odor of rotten eggs. The odor of this gas should not be used as a warning, since its presence may deaden the sense of smell. Hydrogen sulfide can also exist as a liquid at low temperature and high pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen sulfide is a ceiling level of 20 parts of hydrogen sulfide per million parts of air (ppm) or a maximum allowable peak of 50 ppm for 10 minutes once, if no other measurable exposure occurs. NIOSH has recommended that the permissible exposure limit be reduced to 15 mg/m^3 (10 ppm) averaged over a 10-minute period, and that work areas in which the concentration of hydrogen sulfide exceeds 70 mg/m^3 be evacuated. The NIOSH Criteria Document for Hydrogen Sulfide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen sulfide can affect the body if it is inhaled or if it comes in contact with the eyes, skin, nose or throat. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Inhalation of high concentrations of hydrogen sulfide vapor may cause loss of consciousness and death. Inhalation of lower concentrations may cause headache, dizziness, and upset stomach. Exposure to hydrogen sulfide can cause temporary loss of the sense of smell, and irritation of the eyes, nose, or throat.

2. *Long-term Exposure:* Not known.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen sulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen sulfide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and lungs should be stressed.

—Eye disease: Hydrogen sulfide is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Hydrogen sulfide may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen sulfide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Summary of toxicology**

Hydrogen sulfide gas is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations. It irritates the eyes and respiratory tract at low concentrations. Inhalation of high concentrations of hydrogen sulfide, 1000 to 2000 ppm, may cause coma after a single breath and may be rapidly fatal; convulsions may also occur. Exposure to concentrations of hydrogen sulfide above 50 ppm for one hour may produce acute conjunctivitis with pain, lacrimation, and photophobia; in severe form this may progress to keratoconjunctivitis and vesiculation of the corneal epithelium. In low concentrations, hydrogen sulfide may cause headache, fatigue, irritability, insomnia, and gastrointestinal disturbances; in somewhat higher concentrations it affects the central nervous system, causing excitement and dizziness. Prolonged exposure to 250 ppm of hydrogen sulfide may cause pulmonary edema. Prolonged exposure to concentrations of hydrogen sulfide as low as 50 ppm may cause rhinitis, pharyngitis, bronchitis, and pneumonitis. Repeated exposure to hydrogen sulfide results in increased susceptibility, so that eye irritation, cough, and systemic effects may result from concentrations previously tolerated without any effect. Rapid olfactory fatigue can occur at high concentrations.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 34.08
2. Boiling point (760 mm Hg): −60 C (−76 F)
3. Specific gravity (water = 1): Liquid = 1.54
4. Vapor density (air = 1 at 15 C (59 F)): 1.189
5. Melting point: −82.4 C (−116 F)
6. Vapor pressure at 25 C (77 F): 20 atm
7. Solubility in water, g/100 g water at 20 C (68 F): 2.9 (slight)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.

2. Incompatibilities: Contact with strong oxidizers and oxidizing materials may cause fires and explosions. Hydrogen sulfide attacks many metals, which results in the formation of sulfides.

3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur oxides) may be released in a fire involving hydrogen sulfide.

4. Special precautions: Liquid hydrogen sulfide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Hydrogen sulfide is a flammable gas.
2. Autoignition temperature: 260 C (500 F)
3. Flammable limits in air, % by volume: Lower: 4.3; Upper: 46
4. Extinguishant: Alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, hydrogen sulfide can be recognized by the "sense of smell at low concentrations. Odor not reliable at high concentrations, and olfactory fatigue occurs quickly . . . . Threshold is 0.13 ppm. Faint but readily perceptible at 0.77 ppm. Easily noticeable at 4.6 ppm. Strong, unpleasant, but not intolerable at 27 ppm." The *Hygienic Guide* also states that "olfactory fatigue can occur with(in) 2 to 15 minutes at 100 ppm."

2. Eye Irritation Level: Grant states that "effects of hydrogen sulfide on the eyes are notable only at sublethal concentrations, most commonly at concentrations so low that they have no discernible systemic effect . . . . Typically, workmen exposed to low concentrations of hydrogen sulfide gas . . . have no sensation of irritation or discomfort for at least several hours, or sometimes for several days while working in the presence of low concentrations. Ocular symptoms generally start after several hours of exposure and may not appear until the patient has finished his work for the day. There is then gradual onset of a scratchy, irritated sensation in the eyes, with tearing and burning . . . . Experimentally it is demonstrable that at a concentration of 100 ppm in air an immediate irritation of the eyes and respiratory tract is produced, but conditions responsible for the vast majority of cases of hydrogen sulfide keratoconjunctivitis are those in which the concentration is too low to cause immediate irritation and has toxic effect only after several hours or days of exposure. However, in industries where the concentration is regularly kept below 10 ppm in air, it is rare to have any irritation of the eyes."

The *Hygienic Guide* states that "50 to 100 ppm causes slight conjunctivitis and respiratory tract irritation after 1 hour."

3. Evaluation of Warning Properties: Since olfactory fatigue occurs at high concentrations, and since the irritant effects are delayed, hydrogen sulfide is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen sulfide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of hydrogen sulfide. Each measurement should consist of a 10-minute sample or a series of consecutive samples totalling 10 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of hydrogen sulfide in an impinger containing an alkaline suspension of cadmium hydroxide, followed by chemical treatment, and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen sulfide may be used. An analytical method for hydrogen sulfide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid hydrogen sulfide or from contact with vessels containing liquid hydrogen sulfide.
- Any clothing which becomes wet with liquid hydrogen sulfide should be removed immediately and not reworn until the hydrogen sulfide has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid hydrogen sulfide may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen sulfide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from pockets during underground mining operations near sulfide ores	Local exhaust ventilation; respiratory protective devices
Liberation during refining of high-sulfur petroleum	Concentration and recovery of H_2SO_4
Liberation from accumulations of decaying organic matter in sewers and waste waters of tanneries, glue factories, fat-rendering plants, and fertilizer plants	Provide continuous water discharge to sewer and cover and vent waste drains
Liberation as a by-product of dehairing and tanning process	Provide separate sewage lines and cover and vent waste drains; add neutralizing agents ($CaCl_2$) as appropriate; local exhaust ventilation
Liberation during manufacture of viscose rayon	Local exhaust ventilation
Liberation during production of sulfur dyes, carbon disulfide, sulfur, oleum, and thioprene	Local exhaust ventilation or process enclosure
Liberation during vulcanization of rubber; during manufacture of coke from coal having high gypsum content	Local exhaust ventilation or process enclosure
Liberation during excavation projects	Respiratory protective equipment

Liberation in closed containers containing organic matter	Respiratory protective equipment; life-support line

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid hydrogen sulfide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid hydrogen sulfide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen sulfide penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of hydrogen sulfide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If hydrogen sulfide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak to disperse gas.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

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RESPIRATORY PROTECTION FOR HYDROGEN SULFIDE

Condition	**Minimum Respiratory Protection* Required Above 10 ppm**
Gas Concentration	
300 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases or hydrogen sulfide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

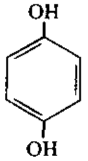
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HYDROQUINONE

INTRODUCTION

This guideline summarizes pertinent information about hydroquinone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_6O_2$
- **Structure:**



- **Synonyms:** 1,4-Benzenediol; dihydroxybenzene; hydroquinol; quinol
- **Identifiers:** CAS 123-31-9; RTECS MX3500000; DOT 2662
- **Appearance and odor:** Colorless to white crystalline solid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110.11
2. Boiling point (at 760 mmHg): 285°C (545°F)
3. Specific gravity (water = 1): 1.332
4. Vapor density (air = 1 at boiling point of hydroquinone): 3.81
5. Melting point: 173°C (344°F)
6. Vapor pressure at 25°C (77°F): 1.8×10^{-5} mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 7
8. Evaporation rate (butyl acetate = 1): 1.8×10^{-6}

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving hydroquinone.
3. Caution: Airborne hydroquinone may be oxidized to quinone ($C_6H_4O_2$) at ordinary room temperatures in the presence of moisture.

- **Flammability**

1. Flash point: 165°C (329°F) (closed cup)
2. Autoignition temperature: 516°C (960°F)
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Combustible solid, Flammability Rating 1 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, hydroquinone should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hydroquinone is 2 milligrams of hydroquinone per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 2 mg/m³ [0.44 parts of hydroquinone per million parts of air (ppm)] as a ceiling concentration determined in any 15-minute sampling period. In those situations in which workers may be exposed to hydroquinone as a component of other materials at a concentration of 5% or less by weight, it should not be necessary to comply with the provisions of the standard; however; protection of workers' health should be insured by avoiding excessive contact with the chemical and by following effective cleaning procedures. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 2 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for hydroquinone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	—	2
NIOSH REL ceiling (15 min)	0.44	2
ACGIH TLV® TWA	—	2

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydroquinone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute subcutaneous injection or oral administration of hydroquinone to multiple species of animals produced hypersensitivity to external stimuli, hyperactive reflexes, breathing difficulty (dyspnea), and bluish discoloration of skin and mucous membranes (due to methemoglobinemia), followed by convulsions, reduced body temperature, paralysis, loss of reflexes, coma, and death (due to decreased oxygen in the blood and respiratory failure). Subchronic or chronic exposure of multiple species of animals by the same routes of administration produced jaundice, anemia, hypoglycemia, increased white blood cell counts, increased cell fragility, depigmentation of skin or fur, and marked weight loss. Subchronic subcutaneous injection of hydroquinone into male rats caused reduction in the weights of sexual organs, sperm production, and fertility (as determined by reduced pregnancies). In mutagenicity tests, hydroquinone damaged DNA and chromosomes in bacteria.
2. *Effects on humans:* Chronic exposure of the eyes to hydroquinone has caused ulceration, opacity, and structural changes.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to hydroquinone can cause headache, dizziness, nausea, vomiting, increased respiration, breathing difficulty, sensation of suffocation, ringing noise in ears, paleness, bluish discoloration of skin, green or brownish-green discoloration of urine, and irritation of the skin and eyes.
2. *Long-term (chronic):* Exposure to hydroquinone can cause depigmentation of the skin, brownish discoloration of the cornea, and blurred vision.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to hydroquinone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, gastrointestinal tract, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to hydroquinone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin and respiratory system.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to hydroquinone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, gastrointestinal tract, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of hydroquinone. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting hydroquinone with cellulose ester membrane filters followed by treatment with aqueous acetic acid and analysis by high-pressure liquid chromatography. A detailed sampling and analytical method for hydroquinone may be found in the *NIOSH Manual of Analytical Methods* (method number 5004).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum) and other appropriate protective clothing necessary to prevent skin contact with hydroquinone.

Workers should be provided with and required to use dust- and splash-proof safety goggles where hydroquinone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with hydroquinone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydroquinone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hydroquinone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with hydroquinone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hydroquinone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to hydroquinone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for hydroquinone

Operations	Controls
During the preparation and use of photographic developers; during use in the dyeing and fur processing industries	Personal protective equipment
During use as an antioxidant; during use as a chemical stabilizer	Local exhaust ventilation, personal protective equipment
During the synthesis of hydroquinone ethers, vitamin E, hydroquinone diacetate, or p-methoxyphenol; during the synthesis and handling of hydroquinone powders	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to hydroquinone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hydroquinone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to hydroquinone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hydroquinone gets on the skin, wash it immediately with soap and water. If hydroquinone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If hydroquinone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Hydroquinone solid may be collected and placed in an appropriate container.
4. Hydroquinone solid or liquid may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.
5. For small quantities of liquids containing hydroquinone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from hydroquinone vapors. Burn the paper in a suitable location away from combustible materials.
6. Large quantities of liquids containing hydroquinone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Hydroquinone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for hydroquinone

Condition	Minimum respiratory protection*†
Concentration: Less than or equal to 50 mg/m³	Any powered air-purifying respirator with a dust filter (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 100 mg/m³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance causes eye irritation or damage—eye protection needed) Any supplied air respirator with tight-fitting facepiece operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 200 mg/m³	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 200 mg/m³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.44 ppm (2 mg/m³) (ceiling).

Occupational Health Guideline for Iodine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: I_2
- Synonyms: None
- Appearance and odor: Violet solid with a sharp, characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for iodine is a ceiling level of 0.1 part of iodine per million parts of air (ppm). This may also be expressed as 1 milligram of iodine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Iodine can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Iodine vapor is a severe irritant of the eyes, respiratory tract, and to a lesser extent, the skin. It may cause severe breathing difficulties which may be delayed in onset. Swallowing iodine may cause burning in the mouth, vomiting, abdominal pain, and diarrhea. Death may result. Crystalline iodine or strong solutions of iodine may cause severe irritation of the skin. It is not easily removed from the skin and may cause burns. An allergic skin rash may occur. It may cause irritation, brown staining, and burning of the eyes.

2. Long-term Exposure: Chronic absorption of iodine may cause insomnia, inflammation of the eyes and nose, bronchitis, tremor, rapid heart beat, diarrhea, and weight loss.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to iodine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to iodine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of thyroid disorders, asthma, allergies, or known sensitization to iodine would be expected to be at increased risk from exposure. Examination of the respiratory tract, eyes, nervous system, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Iodine causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Iodine is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Iodine vapor is a severe irritant of the eyes, respiratory tract, and, to a lesser extent, the skin. Intratracheal administration to dogs of the vapor from 36 mg iodine/kg body weight was fatal after about 3 hours; the animals developed cough, dyspnea, and rales; autopsy findings were pulmonary edema, subpleural hemorrhage, and an increased iodine content of the thyroid

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and urine. Workers exposed to an unspecified concentration experienced a burning sensation in the eyes, lacrimation, blepharitis, rhinitis, stomatitis, and chronic pharyngitis; after accidental exposure in a laboratory, technicians reported headache and a feeling of tightness in the chest. Iodine absorbed by the lungs is changed to iodide and eliminated mainly in the urine; iodine is an essential element in nutrition and is required by the thyroid. Accidental ingestion of 2 to 3 g may be fatal; chronic absorption of iodine causes "iodism," a disease characterized by insomnia, conjunctivitis, rhinitis, bronchitis, tremor, tachycardia, parotitis, diarrhea, and weight loss. In an experimental investigation, four human subjects tolerated 0.57 ppm iodine vapor for 5 minutes without eye irritation, but all experienced eye irritation in 2 minutes at 1.63 ppm. In patients exposed to air saturated with iodine vapor for 3 to 4 minutes for therapeutic purposes, there was brown staining of the corneal epithelium and subsequent spontaneous loss of the layer of tissue; recovery occurred within 2 to 3 days. Iodine in crystalline form or in strong solutions is a severe skin irritant; it is not easily removed from the skin, and the lesions resemble thermal burns. Hypersensitivity to iodine characterized by a skin rash has been reported. Iodine is absorbed through the skin in small amounts from a tincture or from vapor applied to the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 253.8
2. Boiling point (760 mm Hg): 184 C (363 F)
3. Specific gravity (water = 1): 4.9
4. Vapor density (air = 1 at boiling point of iodine): 9
5. Melting point: 113.6 C (237 F)
6. Vapor pressure at 20 C (68 F): 0.3 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of iodine with gaseous or aqueous ammonia forms a water-insoluble solid that is very sensitive to shock when dry and which will explode, causing fires. Contact with acetylene, acetaldehyde, powdered aluminum, or other active metals may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible by itself, but can react vigorously with reducing materials

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of iodine.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "irritation rather than systemic action limits the concentrations of iodine vapor which can be tolerated. An earlier report states that 0.1 ppm is tolerable, whereas 0.3 ppm is not, but no time limits were furnished in the citation. In a recent investigation, four human subjects tolerated 0.57 ppm iodine vapor for 5 minutes without eye irritation, but all experienced eye irritation in 2 minutes at 1.63 ppm." The eye irritation threshold data reported are not consistent.
3. Evaluation of Warning Properties: Since the *Hygienic Guide* states that "the warning properties of iodine vapor are not adequate to prevent excessive inhalation exposure," iodine has been treated as a material with poor warning properties. The ILO also notes that the warning properties of iodine vapor cannot be depended upon to prevent excessive exposure. In addition, a recent investigation has shown that a 5-minute exposure to 0.57 ppm iodine vapor did not produce eye irritation in human subjects.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of iodine. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

At the time of publication of this guideline, no measurement method for iodine had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid iodine or liquids containing more than 7% iodine by weight.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquids containing 7% or less of iodine by weight.
- If employees' clothing has had any possibility of being contaminated with solid iodine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with iodine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of iodine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the iodine, the person performing the operation should be informed of iodine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solid iodine or liquids containing more than 7% iodine by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with iodine should be removed immediately and not reworn until the iodine is removed from the clothing.
- Non-impervious clothing which becomes wet with liquids containing 7% or less of iodine by weight should be removed promptly and not reworn until the iodine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid iodine or liquids containing more than 7% iodine by weight contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where liquids containing 7% or less of iodine by weight may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid iodine or liquids containing more than 7% iodine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with solid iodine or liquids containing more than 7% iodine by weight should be immediately washed or showered with soap or mild detergent and water to remove any iodine.
- Skin that becomes wet with solutions containing 7% or less of iodine by weight should be promptly washed or showered with soap or mild detergent and water to remove any iodine.
- Eating and smoking should not be permitted in areas where solid iodine is handled, processed, or stored.
- Employees who handle solid iodine or liquids containing iodine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to iodine may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of chemical intermediates, pharmaceuticals, photographic chemicals, antiseptics, disinfectants, detergent sanitizers, and organic and inorganic compounds	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a reagent in analytical chemistry; as catalytst in organic synthesis; synthesis of dyes, food additives, and coloring agents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of intermediates in purification of metals; use as a catalyst in the modification of selenium during manufacture of photoelectric cells and rectifiers	Process enclosure; local exhaust ventilation; personal protective equipment
Use during manufacture of specialty lubricants and in production of steriospecific polymers	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If iodine, liquids containing iodine, or strong concentrations of iodine vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If iodine or liquids containing iodine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If iodine or liquids containing iodine penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of iodine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When iodine or liquids containing iodine have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately. (If milk is immediately available, give the person milk instead of water).

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If iodine is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing iodine should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Iodine may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR IODINE

Condition	**Minimum Respiratory Protection* Required Above 0.1 ppm**
Vapor or Particulate Concentration	
1 ppm or 10 mg/m^3 or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or 50 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or 100 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 ppm or 100 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors, acid gases, and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Iron Oxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Fe_2O_3
- Synonyms: Ferric oxide fume
- Appearance: Red-brown fume with a metallic taste

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for iron oxide fume is 10 milligrams of iron oxide fume per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for iron oxide fume a Threshold Limit Value of 5 mg/m³.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Iron oxide fume can affect the body if it is inhaled.

- **Effects of overexposure**

Repeated exposure to iron oxide fume over a period of years may cause x-ray changes of the lungs, but does not cause the exposed person to become ill.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to iron oxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to iron oxide fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Inhalation of iron oxide fume or dust causes an apparently benign pneumoconiosis termed siderosis. Iron oxide alone does not cause fibrosis in the lungs of animals, and the same probably applies to humans. Exposures of 6 to 10 years are usually considered necessary before changes recognizable by x-ray can occur; the retained dust gives x-ray shadows that may be indistinguishable from fibrotic pneumoconiosis. Eight of 25 welders exposed chiefly to iron oxide for an average of 18.7 (range 3 to 32) years had reticulonodular shadows on chest x-rays consistent with siderosis but no reduction in pulmonary function; exposure levels ranged from 0.65 to 47 mg/m³. In another study, 16 welders with an average exposure of 17.1 (range 7 to 30) years also had x-rays suggesting siderosis and spirograms which were normal; however, the static and functional compliance of the lungs was reduced; some of the welders were smokers. The welders with the lowest compliance complained of dyspnea.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 159.7
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Solid = 5.24
4. Vapor density (air = 1 at boiling point of iron oxide fume): Not applicable
5. Melting point: 1566 C (2850 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of iron oxide fume with calcium hypochlorite may cause explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Iron oxide fume is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of iron oxide fume on a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for iron oxide fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to iron oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation in production of steel ingots; processing of iron ore to pig iron; heating and pouring of molten metal in foundry operations; hot rolling sheet and strip steel; fettling of castings in foundry operations; during forging of metal items containing iron/steel; pressing of metal items, grinding and polishing of glass, precious metals, stones, and gem stones	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of iron oxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of iron oxide fume are inadvertantly released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Iron Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR IRON OXIDE FUME

Condition	**Minimum Respiratory Protection* Required Above 10 mg/m^3**
Particulate Concentration	
100 mg/m^3 or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
500 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5,000 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5,000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isoamyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOCH_2CH_2CH(CH_3)_2$
- Synonyms: Banana oil; 3-methyl-1-butanol acetate; 2-methylbutyl ethanoate
- Appearance and odor: Clear, colorless liquid with a banana-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isoamyl acetate is 100 parts of isoamyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 525 milligrams of isoamyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isoamyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to isoamyl acetate may cause irritation of the eyes, nose, and throat. Overexposure may also cause headache, drowsiness, and unconsciousness.
2. *Long-term Exposure:* Prolonged overexposure may cause irritation of the skin.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isoamyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isoamyl acetate at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isoamyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isoamyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Isoamyl acetate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although isoamyl acetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although isoamyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The toxicologic effects of isoamyl acetate are probably similar to those of amyl acetate: chiefly irritation of the conjunctiva and upper respiratory tract, followed by gradual onset of narcosis, with slow recovery after exposure ceases. Men exposed to 950 ppm for 30 minutes reported only irritation of the nose and throat, headache, and weakness; cats exposed to 1900 ppm for 2 to 3 hours per day for a week showed only irritation, weakness, and loss of weight; dogs exposed to 5000 ppm

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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for 1 hour had nasal irritation and drowsiness. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.2
2. Boiling point (760 mm Hg): 145.6 C (294 F)
3. Specific gravity (water = 1): 0.87
4. Vapor density (air = 1 at boiling point of isoamyl acetate): 4.5
5. Melting point: −100 C (−148 F)
6. Vapor pressure at 20 C (68 F): 4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): 0.42

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isoamyl acetate.
4. Special precautions: None

- **Flammability**

1. Flash point: 25 C (77 F) (closed cup)
2. Autoignition temperature: 360 C (680 F)
3. Flammable limits in air, % by volume: Lower: 1.0 (at 100 C (212 F)); Upper: 7.5
4. Extinguishant: Dry chemical, carbon dioxide, foam

- **Warning properties**

1. Odor Threshold: By analogy to amyl acetate, which has an odor threshold of 7 ppm (*Handbook of Industrial Organic Solvents*), the odor of isoamyl acetate is assumed to be detectable below the permissible exposure limit (100 ppm).
2. Eye Irritation Level: The *Handbook of Industrial Organic Solvents* indicates that significant eye and nose irritation does not occur below the threshold limit.
3. Other Information: According to the *Documentation of TLV's*, the "threshold limit of 100 ppm is recommended to prevent significant irritation of the respiratory passages."
4. Evaluation of Warning Properties: For the purposes of this guideline, isoamyl acetate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isoamyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isoamyl acetate may be used. An analytical method for isoamyl acetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isoamyl acetate.
- Clothing wet with liquid isoamyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isoamyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isoamyl acetate, the person performing the operation should be informed of isoamyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid isoamyl acetate should be removed immediately and not reworn until the isoamyl acetate is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid isoamyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isoamyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any isoamyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isoamyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, especially in furniture industry, and on plastic, metal leather, and other surfaces	Local exhaust ventilation; personal protective equipment
Liberation during application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, paper, metal, leather, and other surfaces by dipping, roller coating, tumbling, knifing, or brushing	General dilution ventilation; local exhaust ventilation
Liberation during air or oven-drying of varnishes and lacquers	General dilution ventilation
Liberation during application of cellulosic adhesives by machine spraying, dipping, roller coating, tumbling, knifing, or brushing in shoe manufacturing, book binding, packaging, leather processing, paper processing, and textile	General dilution ventilation; local exhaust ventilation
Liberation during manual application of cellulosic adhesives, including household cements	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during manufacture of shoe polish and furniture polish; during fermentation of whiskey grains	General dilution ventilation
Liberation during manufacture of cellulosic photographic film by formation from solvent solutions	General dilution ventilation; local exhaust ventilation
Liberation during preparation of perfumes, foods, and other materials for use as flavoring or odorant	General dilution ventilation
Liberation during use as an extractant in purification of pharmaceuticals, including penicillin	General dilution ventilation; local exhaust ventilation
Liberation during cleaning and maintenance of acetate-processing equipment, such as kettles, distillation columns, and storage vessels	Personal protective equipment
Liberation during manufacture of bath sponges	General dilution ventilation
Liberation during manufacture of artificial leathers	General dilution ventilation; local exhaust ventilation
Liberation during manufacture of artificial silk, rayon, and pearls; during manufacture and use of bronzing fluids	General dilution ventilation; local exhaust ventilation
Liberation during use in dry cleaning preparations	General dilution ventilation
Use in treating of natural leathers by tanning	General dilution ventilation; local exhaust ventilation; personal protective equipment

Liberation during drying, dry printing, and other finishing processes for textiles; during application of phosphorus in manufacture of fluorescent lamps	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isoamyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isoamyl acetate gets on the skin, promptly flush the contaminated skin with water. If isoamyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isoamyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isoamyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isoamyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isoamyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isoamyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Isoamyl Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Amyl Acetate," *Hygienic Guide Series*, Detroit, Michigan, 1965.
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- Smyth, H. F., and Carpenter, C. P.: "Chemical Burns of the Rabbit Cornea," *American Journal of Ophthalmology*, 29:1363-72, 1946.
- von Oettingen, W. F.: "The Aliphatic Acids and Their Esters: Toxicity and Potential Dangers," *A.M.A. Archives of Industrial Health*, 21:28-65, 1960.

RESPIRATORY PROTECTION FOR ISOAMYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
3000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 3000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isoamyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2CHCH_2CH_2OH$
- Synonyms: 3-Methyl-1-butanol; isobutylcarbinol; isopentyl alcohol; fermentation amyl alcohol; fusel oil
- Appearance and odor: Colorless liquid with an alcoholic odor that causes coughing.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isoamyl alcohol is 100 parts of isoamyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of isoamyl alcohol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isoamyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isoamyl alcohol may cause irritation of the eyes and respiratory tract, headache, dizziness, shortness of breath, cough, nausea, vomiting, and diarrhea. Double vision, deafness, delerium, and death may occur. Coma, sugar in the urine, and blood changes have also been reported.

2. Long-term Exposure: Drying and cracking of the skin may result from prolonged or repeated skin exposure.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isoamyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isoamyl alcohol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isoamyl alcohol exposure.

—Skin disease: Isoamyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although isoamyl alcohol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although isoamyl alcohol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isoamyl alcohol might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isoamyl alcohol vapor is a mild irritant. Among the few reports of experience with the amyl alcohols, exposure of rats to vapor at 8000 ppm was not lethal. Chemically related alcohols are considered to have predominantly narcotic properties at high concentrations. Slight throat irritation has been observed in unacclimated subjects at 100 ppm and objectionable irritation of the eyes, nose, and throat at higher concentrations. No chronic system-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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ic effects from isoamyl alcohol have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 88
2. Boiling point (760 mm Hg): 132 C (270 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of isoamyl alcohol): 3.0
5. Melting point: −117 C (−179 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 2.4
8. Evaporation rate (butyl acetate = 1): 0.2

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isoamyl alcohol.
4. Special precautions: Isoamyl alcohol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 42.8 C (109 F) (closed cup)
2. Autoignition temperature: 350 C (662 F)
3. Flammable limits in air, % by volume (at 212 F): Lower: 1.2; Upper: 9.0
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Quantitative information concerning the odor threshold is not available. The *Handbook of Industrial Solvents,* however, states that the odor of n-amyl alcohol is "apparent at approximately 60 ppm." May reports an odor threshold for amyl alcohol of 35 ppm, and Summer reports 10 ppm. By analogy, it is assumed that the odor of isoamyl alcohol is also below the TLV.
2. Irritation Levels: Patty states that "according to Nelson et al., the following concentrations of 3-methyl-1-butanol (isoamyl alcohol) caused irritation of the respective mucous membranes of the majority of persons subjected to exposure for a few minutes: eyes, 150 ppm (0.54 mg/l); nose, 150 ppm; and throat, 100 ppm (0.36 mg/l)."
3. Evaluation of Warning Properties: Because of its irritant effects and its odor, isoamyl alcohol is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isoamyl alcohol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isoamyl alcohol may be used. An analytical method for isoamyl alcohol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isoamyl alcohol.
- Clothing wet with liquid isoamyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isoamyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isoamyl alcohol, the person performing the operation should be informed of isoamyl alcohol's hazardous properties.
- Non-impervious clothing which becomes wet with liquid isoamyl alcohol should be removed promptly and

not reworn until the isoamyl alcohol is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid isoamyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isoamyl alcohol should be promptly washed or showered with soap or mild detergent and water to remove any isoamyl alcohol.
- Employees who handle liquid isoamyl alcohol should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isoamyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a vehicle, latent, or diluent solvent during application of paints, lacquers, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation
Use in synthesis of drugs and medicinals, as a solvent for alkaloids, and as an extractant of antibiotics in pharmaceutical industry	Local exhaust ventilation; general dilution ventilation
Use in manufacture of lacquers, paints, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in organic synthesis of photographic chemicals, isoamyl acetate, and other esters	Local exhaust ventilation; general dilution ventilation; enclosed process; personal protective equipment
Liberation during manufacture and use of printing inks	Local exhaust ventilation; general dilution ventilation
Use as a solvent for resins, gums, waxes, and oils – perfumes, explosives, shoe cement, analytical determination for fat in milk, and artificial rubber	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during manufacture and use in antifoaming agents and carburing fluids	Local exhaust ventilation; general dilution ventilation
Use in mining industry as a frothing agent for flotation of non-ferrous ores	Local exhaust ventilation; general dilution ventilation
Use as a vehicle solvent for celloidin solutions in microscopy	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isoamyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isoamyl alcohol gets on the skin, promptly flush the contaminated skin with water. If isoamyl alcohol soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isoamyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isoamyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isoamyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isoamyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isoamyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Isoamyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Material Safety Data Sheet – Isoamyl Alcohol*, New York, 1972.

RESPIRATORY PROTECTION FOR ISOAMYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isoamyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

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- Formula: $(CH_3)_2CHCH_2CH_2OH$
- Synonyms: 3-Methyl-1-butanol; isobutylcarbinol; isopentyl alcohol; fermentation amyl alcohol; fusel oil
- Appearance and odor: Colorless liquid with an alcoholic odor that causes coughing.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isoamyl alcohol is 100 parts of isoamyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of isoamyl alcohol per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isoamyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isoamyl alcohol may cause irritation of the eyes and respiratory tract, headache, dizziness, shortness of breath, cough, nausea, vomiting, and diarrhea. Double vision, deafness, delerium, and death may occur. Coma, sugar in the urine, and blood changes have also been reported.

2. Long-term Exposure: Drying and cracking of the skin may result from prolonged or repeated skin exposure.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isoamyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isoamyl alcohol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isoamyl alcohol exposure.

—Skin disease: Isoamyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

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—Kidney disease: Although isoamyl alcohol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isoamyl alcohol might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isoamyl alcohol vapor is a mild irritant. Among the few reports of experience with the amyl alcohols, exposure of rats to vapor at 8000 ppm was not lethal. Chemically related alcohols are considered to have predominantly narcotic properties at high concentrations. Slight throat irritation has been observed in unacclimated subjects at 100 ppm and objectionable irritation of the eyes, nose, and throat at higher concentrations. No chronic system-

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 88
2. Boiling point (760 mm Hg): 132 C (270 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of isoamyl alcohol): 3.0
5. Melting point: −117 C (−179 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 2.4
8. Evaporation rate (butyl acetate = 1): 0.2

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isoamyl alcohol.
4. Special precautions: Isoamyl alcohol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 42.8 C (109 F) (closed cup)
2. Autoignition temperature: 350 C (662 F)
3. Flammable limits in air, % by volume (at 212 F): Lower: 1.2; Upper: 9.0
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

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Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isoamyl alcohol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isoamyl alcohol may be used. An analytical method for isoamyl alcohol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isoamyl alcohol.
- Clothing wet with liquid isoamyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isoamyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isoamyl alcohol, the person performing the operation should be informed of isoamyl alcohol's hazardous properties.
- Non-impervious clothing which becomes wet with liquid isoamyl alcohol should be removed promptly and

not reworn until the isoamyl alcohol is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid isoamyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isoamyl alcohol should be promptly washed or showered with soap or mild detergent and water to remove any isoamyl alcohol.
- Employees who handle liquid isoamyl alcohol should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isoamyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a vehicle, latent, or diluent solvent during application of paints, lacquers, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation
Use in synthesis of drugs and medicinals, as a solvent for alkaloids, and as an extractant of antibiotics in pharmaceutical industry	Local exhaust ventilation; general dilution ventilation
Use in manufacture of lacquers, paints, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in organic synthesis of photographic chemicals, isoamyl acetate, and other esters	Local exhaust ventilation; general dilution ventilation; enclosed process; personal protective equipment
Liberation during manufacture and use of printing inks	Local exhaust ventilation; general dilution ventilation
Use as a solvent for resins, gums, waxes, and oils— perfumes, explosives, shoe cement, analytical determination for fat in milk, and artificial rubber	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during manufacture and use in antifoaming agents and carburing fluids	Local exhaust ventilation; general dilution ventilation
Use in mining industry as a frothing agent for flotation of non-ferrous ores	Local exhaust ventilation; general dilution ventilation
Use as a vehicle solvent for celloidin solutions in microscopy	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isoamyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isoamyl alcohol gets on the skin, promptly flush the contaminated skin with water. If isoamyl alcohol soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isoamyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isoamyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isoamyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isoamyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isoamyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Isoamyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
- *Handbook of Organic Industrial Solvents*, Technical Guide No. 6 (4th ed.), American Mutual Insurance Alliance, Chicago, 1972.
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RESPIRATORY PROTECTION FOR ISOAMYL ALCOHOL

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isobutyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOCH_2CH(CH_3)_2$
- Synonyms: 2-Methylpropyl acetate; beta-methylpropyl ethanoate; acetic acid isobutyl ester
- Appearance and odor: Clear, colorless liquid with a pleasant, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isobutyl acetate is 150 parts of isobutyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 700 milligrams of isobutyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isobutyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isobutyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isobutyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isobutyl acetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isobutyl acetate exposure.

—Skin disease: Isobutyl acetate is a mild defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although isobutyl acetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isobutyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although isobutyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The principal effects of overexposure to isobutyl acetate are irritation of the eyes and nose. Narcosis occurs at high concentrations. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 116
  2. Boiling point (760 mm Hg): 117 C (243 F)

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National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Specific gravity (water = 1): 0.87
4. Vapor density (air = 1 at boiling point of isobutyl acetate): 4.0
5. Melting point: −97 C (−143 F)
6. Vapor pressure at 20 C (68 F): 13 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.67
8. Evaporation rate (butyl acetate = 1): 1.5

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isobutyl acetate.
4. Special precautions: Isobutyl acetate will dissolve a wide variety of resins and plastics.

- **Flammability**

1. Flash point: 18 C (64 F) (closed cup)
2. Autoignition temperature: 421 C (790 F)
3. Flammable limits in air, % by volume: Lower: 2.4; Upper: 10.5
4. Extinguishant: Dry chemical, carbon dioxide, foam

- **Warning properties**

1. Odor Threshold: Summer and May both report an odor threshold for isobutyl acetate of 4 ppm.
2. Eye Irritation Level: According to the *Documentation of TLV's*, the TLV of 150 ppm "is recommended primarily to prevent irritation of eyes and respiratory passages."
3. Evaluation of Warning Properties: Since the odor threshold of isobutyl acetate is below the permissible exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isobutyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isobutyl acetate may be used. An analytical method for isobutyl acetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isobutyl acetate.
- Clothing wet with liquid isobutyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isobutyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isobutyl acetate, the person performing the operation should be informed of isobutyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid isobutyl acetate should be removed immediately and not reworn until the isobutyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isobutyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isobutyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any isobutyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isobutyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, plastic, metal, leather, and other surfaces	Local exhaust ventilation; personal protective equipment
Liberation during application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, paper, metal, leather, and other surfaces by dipping, roller coating, tumbling, knifing, or brushing	Local exhaust ventilation; general dilution ventilation
Liberation during oven backing of phenolic and epoxy coatings	General dilution ventilation
Liberation during application of nitrocellulose, cellulose acetate, cellulose acetate butyrate, and cyclized rubber adhesives by machine spraying, dipping, roller coating, tumbling, knifing, or brushing in shoe manufacturing, book binding, packaging, leather processing, photographic film manufacturing, and paper processing	Local exhaust ventilation; general dilution ventilation
Use and liberation during manual application of nitrocellulose, cellulose acetate, cellulose acetate butyrate, and cyclized rubber adhesives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during cleaning and maintenance of acetate-processing equipment, including kettles, distillation columns, and storage vessels	Personal protective equipment
Liberation during manufacture of some perfumes, cosmetics, and flavoring agents	General dilution ventilation
Liberation during spray application of vinyl-based primers, maintenance paints, and other industrial coatings	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isobutyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isobutyl acetate gets on the skin, promptly flush the contaminated skin with water. If isobutyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isobutyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isobutyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isobutyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isobutyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isobutyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Isobutyl Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
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- von Oettingen, W. F.: "The Aliphatic Acids and Their Esters: Toxicity and Potential Dangers," *A.M.A. Archives of Industrial Health*, 21:28-65, 1960.

RESPIRATORY PROTECTION FOR ISOBUTYL ACETATE

Condition	**Minimum Respiratory Protection*** **Required Above 150 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
7500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 7500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isobutyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2CHCH_2OH$
- Synonyms: Isobutanol; IBA; 2-methyl-1-propanol; isopropylcarbinol
- Appearance and odor: Colorless liquid with a mild, non-residual odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isobutyl alcohol is 100 parts of isobutyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of isobutyl alcohol per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for isobutyl alcohol a Threshold Limit Value of 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isobutyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isobutyl alcohol may cause irritation of the eyes, nose, and throat, headache, dizziness, and drowsiness.

2. Long-term Exposure: Drying and cracking of the skin may result from prolonged skin exposure.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isobutyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isobutyl alcohol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isobutyl alcohol exposure.

—Skin disease: Isobutyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although isobutyl alcohol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although isobutyl alcohol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isobutyl alcohol might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isobutyl alcohol vapor had a narcotic effect in high concentrations (6400 ppm) for mice, and was lethal at 10,000 to 15,000 ppm. In employees, repeated exposures at 100 ppm had no significant effect, although irritation of the eyes and throat were observed in other studies where the vapor concentrations were higher. Isobutyl alcohol is a mild skin irritant. No chronic systemic effects have been reported in humans.

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National Institute for Occupational Safety and Health

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Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74
2. Boiling point (760 mm Hg): 108 C (226 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of isobutyl alcohol): 2.6
5. Melting point: −108 C (−162 F)
6. Vapor pressure at 20 C (68 F): 8.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.7
8. Evaporation rate (butyl acetate = 1): 0.82

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isobutyl alcohol.
4. Special precautions: Isobutyl alcohol will attack some forms of plastics, rubber, and coatings. It may react with metallic aluminum at high temperatures.

- **Flammability**

1. Flash point: 27.8 C (82 F) (closed cup)
2. Autoignition temperature: 427 C (800 F)
3. Flammable limits in air, % by volume (at 212 F): Lower: 1.2; Upper: 10.9
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold of 40 ppm.
2. Eye Irritation Level: Patty states, "Fassett has studied isobutyl alcohol under the same conditions of exposure as for n-butyl alcohol. No evidence of eye irritation was noted with repeated 8-hour exposures to levels on the order of 100 ppm. Animal data showed that it was very similar to n-butyl alcohol in its effects." n-Butyl alcohol is known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of isobutyl alcohol is below the permissible exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isobutyl alcohol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isobutyl alcohol may be used. An analytical method for isobutyl alcohol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isobutyl alcohol.
- Clothing wet with liquid isobutyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isobutyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isobutyl alcohol, the person performing the operation should be informed of isobutyl alcohol's hazardous properties.
- Any clothing which becomes wet with liquid isobutyl alcohol should be removed immediately and not reworn until the isobutyl alcohol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isobutyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isobutyl alcohol should be promptly washed or showered to remove any isobutyl alcohol.
- Employees who handle liquid isobutyl alcohol should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isobutyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray applications of nitrocellulose lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of industrial cleaners; during use of paint removers	General dilution ventilation; personal protective equipment
Liberation during hand application of nitrocellulose lacquers; during manufacture of lubricating oil and hydraulic fluids; during manufacture of amino resins and plasticizers	General dilution ventilation
Use during manufacture of nitrocellulose lacquers, paint removers, and industrial cleaners	General dilution ventilation; personal protective equipment
Liberation during manufacture of acetaldehyde; during distillation of whiskey	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isobutyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isobutyl alcohol gets on the skin, promptly flush the contaminated skin with water. If isobutyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isobutyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isobutyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isobutyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isobutyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isobutyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ISOBUTYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

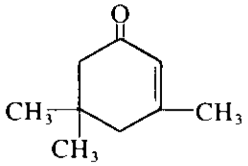
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ISOPHORONE

INTRODUCTION

This guideline summarizes pertinent information about isophorone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_9H_{14}O$
- **Structure:**



- **Synonyms:** Isoacetophorone; isoforon; 3,5,5-trimethyl-2-cyclohexene-l-one
- **Identifiers:** CAS 78-59-1; RTECS GW7700000; DOT not assigned
- **Appearance and odor:** Colorless to pale yellow liquid with an odor like peppermint or camphor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 138.23
2. Boiling point (at 760 mmHg): 215°C (419°F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of isophorone): 4.77
5. Melting point: -8.1°C (17°F)
6. Vapor pressure at 20°C (68°F), 0.26 mmHg; at 25°C (77°F), 0.44 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.2
8. Evaporation rate (butyl acetate = 1): 0.03
9. Saturation concentration in air (approximate): At 20°C (68°F), 0.034% (340 ppm); at 25°C (77°F), 0.06% (600 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving isophorone.
3. Caution: Isophorone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 84.4°C (184°F) (closed cup)
2. Autoignition temperature: 460°C (860°F)
3. Flammable limits in air, % by volume: Lower, 0.8; upper, 3.8
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.2 ppm
2. Eye irritation level: 25 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, isophorone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for isophorone is 25 parts of isophorone per million parts of air (ppm) [140 milligrams of isophorone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) over an 8-hour workshift. The NIOSH REL is 4 ppm (23 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value ceiling (TLV®-C), the concentration that should not be exceeded during any part of the working exposure, is 5 ppm (25 mg/m^3) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for isophorone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	25	140
NIOSH REL TWA	4	23
ACGIH TLV®-ceiling	5	25

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isophorone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute inhalation of isophorone by rats caused narcosis and death. Subchronic inhalation of isophorone by guinea pigs and rats caused injury to the kidneys (congestion, dilated Bowman's capsules, or cloudy swelling of convoluted tubules) and lungs (congestion, hemorrhage, desquamation, or pneumonia).

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to isophorone can cause depressed appetite and body weight, headache, dizziness, fatigue, nausea, and diarrhea. Irritation of the skin, eyes, and upper and lower respiratory tracts can also occur.
2. *Long-term (chronic):* Exposure to isophorone can cause drying, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to isophorone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to isophorone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease, concurrent dermatitis, and significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional frequent examinations may be necessary should a worker develop symptoms that may be attributed to exposure to isophorone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to isophorone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting isophorone vapors with a charcoal tube followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure isophorone may also be used if available. A detailed sampling and analytical method for isophorone may be found in the *NIOSH Manual of Analytical Methods* (method number 2508).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with isophorone.

Workers should be provided with and required to use splash-proof safety goggles where isophorone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with isophorone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of isophorone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of isophorone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with isophorone should be promptly washed with soap and water.

Workers who handle isophorone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle isophorone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to isophorone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for isophorone

Operations	Controls
During use as a solvent in the manufacture of vinyl resins, nitrocellulose, fats, chlorinated rubber, herbicides, coatings, roll-coating finishes, siding, paint, adhesives, and inks	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in organic synthesis in the manufacture of lubricating oil additives, fungicides, and tetramethylquanidine	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to isophorone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If isophorone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to isophorone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If isophorone gets on the skin, wash it immediately with soap and water. If isophorone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If isophorone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing isophorone, absorb on paper towels and place in an appropriate container. Place towels in a safe place (such as a fume hood) for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from isophorone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing isophorone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Isophorone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing isophorone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for isophorone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 40 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 100 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 200 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied air respirator with a tight-fitting facepiece and operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 800 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 800 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 4 ppm (23 mg/m^3) (TWA).

Occupational Health Guideline for Isopropyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOCH(CH_3)_2$
- Synonyms: Isopropyl ester of acetic acid; sec-propyl acetate
- Appearance and odor: Colorless liquid with a fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropyl acetate is 250 parts of isopropyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 950 milligrams of isopropyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isopropyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isopropyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropyl acetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isopropyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Isopropyl acetate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although isopropyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although isopropyl acetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isopropyl acetate irritates the eyes and upper respiratory tract. It may produce narcosis at high concentrations approaching the lethal level in animals. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 102
  2. Boiling point (760 mm Hg): 90 C (194 F)

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Specific gravity (water = 1): 0.87

4. Vapor density (air = 1 at boiling point of isopropyl acetate): 3.5

5. Melting point: −69 C (−92 F)

6. Vapor pressure at 20 C (68 F): 43 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 2.9

8. Evaporation rate (butyl acetate = 1): 5

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, or strong acids may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isopropyl acetate.

4. Special precautions: Isopropyl acetate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 4.4 C (40 F) (closed cup)

2. Autoignition temperature: 460 C (860 F)

3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 8.0

4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports two odor thresholds for isopropyl acetate: 30 ppm and 400 ppm.

2. Eye Irritation Level: Patty reports that 200 ppm causes eye irritation in man.

3. Evaluation of Warning Properties: Because of its low thresholds of odor and eye irritation, isopropyl acetate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isopropyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isopropyl acetate may be used. An analytical method for isopropyl acetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isopropyl acetate.
- Clothing wet with liquid isopropyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropyl acetate, the person performing the operation should be informed of isopropyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid isopropyl acetate should be removed immediately and not reworn until the isopropyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isopropyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isopropyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any isopropyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during coating application to artificial silk, leather, and vinyl resin fabrics	Local exhaust ventilation; general dilution ventilation
Liberation during use as a vehicle solvent during spray application of cellulose nitrate and ethyl cellulose lacquers	Local exhaust ventilation; spray booths; personal protective equipment
Liberation during manufacture of cellulose nitrate and ethyl cellulose lacquers and thinners	Local exhaust ventilation; general dilution ventilation
Use as a solvent of synthetic resins in plastics industry	Local exhaust ventilation; general dilution ventilation
Liberation during manufacture and use of printing and litho inks; during manufacture of perfumes and flavoring agents	Local exhaust ventilation; general dilution ventilation
Use as a general solvent for waxes, gums, and oils	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isopropyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isopropyl acetate gets on the skin, promptly flush the contaminated skin with water. If isopropyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isopropyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isopropyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isopropyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isopropyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isopropyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ISOPROPYL ACETATE

Condition	**Minimum Respiratory Protection* Required Above 250 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
12,500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
16,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 16,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isopropyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CHOHCH_3$
- Synonyms: Isopropanol; IPA; 2-propanol; sec-propyl alcohol
- Appearance and odor: Colorless liquid with an odor of rubbing alcohol.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropyl alcohol is 400 parts of isopropyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 980 milligrams of isopropyl alcohol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 400 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 800 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Isopropyl Alcohol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to high air concentrations of isopropyl alcohol may cause mild irritation of the eyes, nose, and throat. Drowsiness, headache, and incoordination may also occur. Swallowing isopropyl alcohol may cause drowsiness, unconsciousness, and death. Gastrointestinal pain, cramps, nausea, vomiting, and diarrhea may also result from swallowing this alcohol.

2. Long-term Exposure: Drying and cracking of the skin may result from prolonged skin exposure. Epidemiological investigations have established that a carcinogenic substance is present in isopropyl alcohol manufacturing areas, but have not confirmed isopropyl alcohol as a causative agent of cancer.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isopropyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropyl alcohol at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, and respiratory system should be stressed.

—Skin disease: Isopropyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although isopropyl alcohol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although isopropyl alcohol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropyl

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alcohol might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The most important toxic effect of isopropyl alcohol is narcosis, which occurs in mice at vapor concentrations of 3000 ppm, the effects increasing with the duration of exposure. Exposure to higher concentrations results in ataxia, followed by deep narcosis and death. Reversible changes occurred in the liver fat of mice repeatedly exposed to high concentrations of vapor. Isopropyl alcohol is metabolized fairly rapidly, and acetone may be detected in the urine following heavy exposures. Human volunteers reported mild irritation of the eyes, nose, and throat after 3 to 5 minutes exposure to vapor at 400 ppm; at 800 ppm the results were not severe, but most subjects found the atmosphere to be objectionable. Accidental, extensive wetting of the skin could occur in industrial situations and as isopropyl alcohol is absorbed readily through the skin, the additive effect of inhalation and skin absorption could have serious results. Similarly, there is a risk of deliberate ingestion of isopropyl alcohol as a substitute for ethyl alcohol, which would add to the effects of inhalation. The defatting action of isopropyl alcohol can cause mild skin irritation, but a small percentage of workers may develop contact dermatitis of a more serious nature. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60
2. Boiling point (760 mm Hg): 82 C (180 F)
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of isopropyl alcohol): 2.1
5. Melting point: −89 C (−128 F)
6. Vapor pressure at 20 C (68 F): 33 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 2.83

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isopropyl alcohol.
4. Special precautions: Isopropyl alcohol will attack some forms of plastics, rubber, and coatings. It may also react with metallic aluminum at high temperatures.

- **Flammability**

1. Flash point: 12 C (53 F) (closed cup)
2. Autoignition temperature: 399 C (750 F)
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 12.0
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty reports, "Scherberger et al. stated that the concentration with identifiable odor of isopropyl alcohol is 200 ppm." May reports an odor threshold of 45 ppm.
2. Irritation Level: According to Patty, "mild irritation of the eyes, nose, and throat was induced in human subjects exposed by Nelson and associates for 3 to 5 minutes to 400 ppm of isopropyl alcohol."
3. Evaluation of Warning Properties: Through its odor and irritant effects, isopropyl alcohol can be detected below or at the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of isopropyl alcohol. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of isopropyl alcohol vapors using an adsorption tube with subsequent desorption with 2-butanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isopropyl alcohol may be used. An analytical method for isopropyl alcohol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isopropyl alcohol.
- Any clothing which becomes wet with liquid isopropyl alcohol should be removed immediately and not reworn until the isopropyl alcohol is removed from the clothing.
- Clothing wet with liquid isopropyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropyl alcohol, the person performing the operation should be informed of isopropyl alcohol's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isopropyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isopropyl alcohol should be promptly washed or showered to remove any isopropyl alcohol.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in spray and heat applications of surface coatings, including stain, varnish, nitrocellulose lacquers, and quick-drying inks and paints	General dilution ventilation; personal protective equipment
Use as a solvent in application other than spray or heat of surface coatings, including stain, varnish, nitrocellulose lacquers, quick-drying inks and paints, textile coatings and dyes, dopes, and polishes	General dilution ventilation; personal protective equipment
Use in manufacture and liberation during packing of acetone	General dilution ventilation; personal protective equipment
Use as a solvent in manufacture of surface coatings and thinners	General dilution ventilation; personal protective equipment
Use in organic synthesis for isopropyl derivatives, including phenols, acetates, xanthates, ether, amines, myristate, palmitate, nitrite, and glycerin	General dilution ventilation; personal protective equipment
Use in manufacture of cosmetics, including liniments, skin lotions, permanent wave lotions, and color hair rinses	General dilution ventilation; personal protective equipment
Liberation during use as a disinfectant and sanitizer; use during cleaning and degreasing operations	General dilution ventilation; personal protective equipment
Use in preparation, manufacture, and packaging of disinfectants and sanitizers, including rubbing alcohol, other antiseptic solutions, skin astringents, mouth washes, and medicated sprays	General dilution ventilation; personal protective equipment

Operation	Controls
Use in manufacture of cleaning and degreasing agents, including stain and spot removers, glass cleaners, rug and uphostery cleaning, tar remover, liquid soap, and windshield cleaner fluid; use in manufacture of de-icing, de-fogging, and anti-freeze products	General dilution ventilation; personal protective equipment
Use in extraction and purification of alkaloids, proteins, chlorophyll, perfumes, sulfuric acid, vitamins, kelp, pectin, resins, gums, and waxes	General dilution ventilation; personal protective equipment
Use in manufacture of rubber products; use as an additive in anti-stalling gasoline, lubricants, denatured ethyl alcohol, hydraulic brake fluids, and rocket fuel	General dilution ventilation; personal protective equipment
Use in manufacture of adhesives, including nitrocellulose film and microfilm cement; use in manufacture of safety glass	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isopropyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isopropyl alcohol gets on the skin, flush the contaminated skin with water. If isopropyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isopropyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isopropyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isopropyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Isopropyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Isopropyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ISOPROPYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 400 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
20,000 ppm or less	A gas mask with a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 20,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isopropylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2CHNH_2$
- Synonyms: Monoisopropylamine; 2-aminopropane
- Appearance and odor: Colorless liquid with a pungent, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropylamine is 5 parts of isopropylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of isopropylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropylamine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Isopropylamine vapor may cause irritation of the nose, throat, and lungs. Both isopropylamine liquid and vapor may cause irritation or burning of the eyes and skin. Permanent eye damage may occur if proper care is not given immediately. Breathing difficulties may occur either immediately or may be delayed.
2. *Long-term Exposure:* Repeated or prolonged exposure to isopropylamine causes an irritation of the skin.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isopropylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropylamine at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isopropylamine exposure.

—Chronic respiratory disease: Isopropylamine causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropylamine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Isopropylamine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Isopropylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isopropylamine vapor is a respiratory and eye irritant. Rats exposed to 8000 ppm for 4 hours died as a result of pulmonary edema. Human subjects experienced irritation of the nose and throat after brief exposures to 10 to 20 ppm. Workers complained of transient visual disturbances after exposure to the vapor for 8 hours, probably due to mild corneal edema that usually cleared within 3 or 4 hours. The liquid is capable of causing very severe eye burns, which may cause permanent visual impairment. Isopropylamine in both liquid and vapor forms is irritating to the skin and may cause skin burns; repeated lesser exposures may result in dermatitis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 59.1
2. Boiling point (760 mm Hg): 32.4 C (90 F)
3. Specific gravity (water = 1): 0.68
4. Vapor density (air = 1 at boiling point of isopropylamine): 2.03
5. Melting point: −95 C (−139 F)
6. Vapor pressure at 20 C (68 F): 478 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid isopropylamine with strong acids will cause explosive spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving isopropylamine.
4. Special precautions: Liquid isopropylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −37 C (−35 F) (closed cup)
2. Autoignition temperature: 402 C (756 F).
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 10.4
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Patty reports that at a concentration of 5 to 10 ppm, the ammoniacal odor is definite, and at 10 to 20 ppm, the odor is strong.
2. Eye Irritation Level: The MCA Chemical Safety Data Sheet notes that the vapors of isopropylamine are highly irritating to the eyes, but no quantitative information is available concerning the threshold of eye irritation.
3. Other Information: Patty reports that nose and throat irritation results from short exposures to 10 to 20 ppm isopropylamine. No eye irritation is cited.
4. Evaluation of Warning Properties: Since the odor of isopropylamine is definite at a concentration which is only twice the permissible exposure, and since nose and throat irritation occurs at a concentration which is only 2 to 4 times the permissible exposure, isopropylamine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of isopropylamine in a bubbler containing sulfuric acid, followed by treatment with sodium hydroxide, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isopropylamine may be used. An analytical method for isopropylamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid isopropylamine, where skin contact may occur.
- Clothing wet with liquid isopropylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropylamine, the person performing the operation should be informed of isopropylamine's hazardous properties.
- Where exposure of an employee's body to liquid isopropylamine may occur, facilities for quick drench-

ing of the body should be provided within the immediate work area for emergency use.

- Any clothing which becomes wet with isopropylamine or non-impervious clothing which becomes contaminated with isopropylamine should be removed immediately and not reworn until the isopropylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid isopropylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid isopropylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid isopropylamine should be immediately washed or showered to remove any isopropylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use as an intermediate in synthesis of agricultural chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solubilizer for 2,4-D and 2,4,5-T herbicides in hard water	Local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of insecticides and bactericides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use with surface-active sulfonate to form oil-soluble emulsifier and detergent for use in dry cleaning operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of vulcanization accelerators for sulfur-cured rubbers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of ore flotation agents; use as a depilatory on skins and hides in leather manufacture; use in manufacture of emulsion-type floor polish	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a general solvent; use as a stabilizer against oxidation and polymerization	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of medicinals in purification of penicillin and streptomycin; use as an intermediate in synthesis of some dyes	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If isopropylamine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If isopropylamine gets on the skin, immediately flush the contaminated skin with water. If isopropylamine soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of isopropylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isopropylamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isopropylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Isopropylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Isopropylamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Isopropylamine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-72, Isopropylamine,* Washington, D.C., 1959.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Isopropylamine*, New York, 1971.

RESPIRATORY PROTECTION FOR ISOPROPYLAMINE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
250 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing protection against isopropylamine. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against isopropylamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
4000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against isopropylamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Isopropylether

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $((CH_3)_2CH)_2O$
- Synonyms: Diisopropyl ether; 2-isopropoxypropane
- Appearance and odor: Colorless liquid with a sharp, sweet, ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropylether is 500 parts of isopropylether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2100 milligrams of isopropylether per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for isopropylether a Threshold Limit Value of 250 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropylether can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Strong concentrations of isopropylether vapors may cause irritation of the eyes and nose. Animal experiments suggest that exposure to high concentrations of this chemical may cause drowsiness, dizziness, and unconsciousness.

2. Long-term Exposure: Repeated or prolonged exposure to liquid isopropylether may cause dryness and irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to isopropylether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropylether at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from isopropylether exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropylether might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Isopropylether is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isopropylether vapor is a mild irritant of the eyes and mucous membranes; high levels cause narcosis in animals. Animals exposed to 30,000 ppm for 1 hour showed signs of narcosis. Exposure of human subjects to 800 ppm for 5 minutes caused irritation of the eyes and nose and some reported respiratory discomfort; exposure to 500 ppm for 15 minutes was not irritating, but at 300 ppm one third of the subjects objected to the unpleasant odor. The liquid dropped in the eye of a rabbit caused minor injury. In rabbits, repeated skin exposure to the liquid for 10 days caused dermatitis, possibly due to defatting action.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.2
2. Boiling point (760 mm Hg): 68.9 C (156 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of isopropylether): 3.5
5. Melting point: −85 C (−121 F)
6. Vapor pressure at 20 C (68 F): 119 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): 8

- **Reactivity**

1. Conditions contributing to instability: Contact with air causes formation of explosive peroxides that may detonate when heated or subjected to shock.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving isopropylether.
4. Special precautions: Isopropylether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −27.8 C (−18 F) (closed cup)
2. Autoignition temperature: 443 C (830 F)
3. Flammable limits in air, % by volume: Lower: 1.4; Upper: 7.9
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that 35% of human subjects exposed experimentally to isopropylether "objected to the unpleasant odor of this solvent at a vapor concentration of 300 ppm."
2. Irritation Level: Patty states that "Silverman et al. reported that humans exposed to a vapor concentration of 500 ppm isopropyl ether for 15 minutes while watching a movie noted no irritating properties . . . . At 800 ppm for 5 minutes most subjects reported irritation of the eyes and nose, and the most sensitive reported respiratory discomfort."
3. Evaluation of Warning Properties: Through its odor and irritant effects, isopropylether can be detected at or slightly above the permissible exposure limit.

For the purposes of this guideline, therefore, isopropylether is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isopropylether may be used. An analytical method for isopropylether is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid isopropylether.

- Clothing wet with isopropylether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropylether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropylether, the person performing the operation should be informed of isopropylether's hazardous properties.
- Any clothing which becomes wet with liquid isopropylether should be removed immediately and not reworn until the isopropylether is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isopropylether may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isopropylether should be promptly washed or showered with soap or mild detergent and water to remove any isopropylether.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropylether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in extraction processes, rubber adhesives, lacquers, resins, oils, cellulose, pharmaceutical manufacture, smokeless gunpowder, and textile spot cleaning	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis as an alkylation agent; emulsion breaker in petroleum industry; and as blending agent for gasoline	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid isopropylether gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid isopropylether gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid isopropylether soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of isopropylether, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When isopropylether has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If isopropylether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Isopropylether should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of isopropylether vapors are permitted.

- Waste disposal method:

Isopropylether may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Isopropylether," *Documentation of the Threshold Limit Values for Substances in Workroom Air*

(3rd ed., 2nd printing), Cincinnati, 1974.

- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Isopropylether*, New York, 1968.

RESPIRATORY PROTECTION FOR ISOPROPYLETHER

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

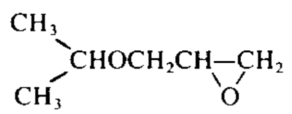
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ISOPROPYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about isopropyl glycidyl ether (IGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{12}O_2$
- **Structure:**



- **Synonyms:** 1,2-epoxy-3-isopropoxypropane; glycidyl isopropyl ether; IGE; (isopropoxymethyl)oxirane; isopropyl epoxypropyl ether
- **Identifiers:** CAS 4016-14-2; RTECS TZ3500000; DOT not assigned
- **Appearance:** Colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.18
2. Boiling point (at 760 mmHg): 137 °C (270 °F)
3. Specific gravity (water = 1): 0.9
4. Vapor density (air = 1 at boiling point of IGE): 4.0
5. Vapor pressure at 25 °C (77 °F): 9.4 mmHg
6. Solubility in water, g/100 g water at 20 °C (68 °F): 18.8
7. Evaporation rate (butyl acetate = 1): 0.99
8. Saturation concentration in air (approximate) at 25 °C (77 °F): 1.237% (12.370 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with strong caustics may cause polymerization. IGE should not be exposed to air or light because explosive peroxides may be formed.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving IGE.
3. Caution: IGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 33 °C (92 °F) (closed cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class IC Flammable Liquid (29 CFR 1910.106)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, IGE should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for IGE is 50 parts of IGE per million parts of air (ppm) [240 milligrams of IGE per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 50 ppm (240 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (240 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 75 ppm (360 mg/m³) (Table 1).

Table 1.—Occupational exposure limits for isopropyl glycidyl ether

	Exposure limits	
	ppm	**mg/m³**
OSHA PEL TWA	50	240
NIOSH REL ceiling (15 min)	50	240
ACGIH TLV® TWA	50	240
STEL	75	360

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

IGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute oral administration of IGE to mice, rats, and rabbits caused central nervous system depression. Subchronic inhalation of IGE by rats caused decreased weight gain, inflammation of the lungs, pneumonia, and respiratory distress.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to IGE can cause mental confusion and moderate irritation of the eyes, skin, and respiratory tract.
2. *Long-term (chronic):* Exposure to IGE can cause dermatitis and skin sensitization.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to IGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to IGE at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to IGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of IGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting IGE vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure IGE may also be used if available. A detailed sampling and analytical method for IGE may be found in the *NIOSH Manual of Analytical Methods* (method number S77).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum) and other appropriate protective clothing necessary to prevent skin contact with IGE.

Workers should be provided with and required to use splash-proof safety goggles where IGE may come in contact with the eyes.

SANITATION

Clothing which is contaminated with IGE should be removed immediately and placed in closed containers for storage until provision is made for the removal of IGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of IGE's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with IGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle IGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to IGE may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for isopropyl glycidyl ether

Operations	Controls
During use as a reactive diluent for epoxy resins; during use as a chemical intermediate for the synthesis of esters and ethers	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a stabilizing agent for organic chemicals	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to IGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If IGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to IGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If IGE gets on the skin, wash it immediately with soap and water. If IGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If IGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing IGE, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from IGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing IGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. IGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing IGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flash back prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for isopropyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 1,500 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 1,500 ppm	Any self-contained breathing apparatus with a full facepiece and operated in pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 50 ppm (240 mg/m^3) (ceiling).

Occupational Health Guideline for Ketene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2CO
- Synonyms: None
- Appearance and odor: Colorless gas with a sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ketene is 0.5 parts of ketene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.9 milligrams of ketene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ketene can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to ketene may cause irritation of the eyes, nose, throat, and lungs. It may also cause cough, chest pain, and severe breathing difficulty. This may occur several hours after exposure and may be severe enough to cause death.
2. *Long-term Exposure:* Chronic overexposure to ketene may cause permanent lung damage.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ketene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ketene at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ketene causes lung damage in animals.

—FVC and FEV (1 sec): Ketene is a severe pulmonary irritant in animals.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Ketene is a severe respiratory irritant. Concentrations over 100 ppm were invariably fatal to mice, rats, and guinea pigs; death occurred rapidly with symptoms of marked eye, nose, throat, and pulmonary irritation; autopsies showed major damage to alveolar walls with pulmonary edema. The LC50 for mice was established at 17 ppm for 10 minutes, but 1 ppm was tolerated without apparent chronic injury by several animal species exposed for 6 hours daily for 6 months. Although it has not been reported in humans, animal data indicate that chronic pulmonary changes (emphysema and fibrosis) may result from repeated acute exposures.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 42
  2. Boiling point (760 mm Hg): −56 C (−69 F)
  3. Specific gravity (water = 1): Not applicable

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Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Vapor density (air = 1 at boiling point of ketene): 1.45

5. Melting point: −151 C (−239 F)

6. Vapor pressure at 20 C (68 F): Not pertinent

7. Solubility in water, g/100 g water at 20 C (68 F): Reacts with water to form acetic acid

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Ketene reacts vigorously with water and with a wide variety of organic compounds.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ketene.

4. Special precautions: Dimerization of ketene to diketene occurs even at low temperatures.

- **Flammability**

1. Flash point: Not applicable (gas)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Stop flow of gas

- **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: Grant states that "exposure of monkeys to 23 ppm in air for 4 hours caused the animals to rub their eyes, cough, and become lethargic . . . . The dimer, diketene, is said to be lacrimatory and to cause marked irritation of the conjunctiva."

3. Evaluation of Warning Properties: Since there is no quantitative information relating its warning properties to air concentrations, ketene is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ketene in a bubbler containing alkaline hydroxlammonium chloride, followed by treatment with ferric chloride, and colorimetric analysis. An analytical method for ketene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ketene may occur and control methods which may be effective in each case:

Operation	Controls
Use as an intermediate in production of acetic anhydride, cellulose and vinyl acetate resins and plastics, acrylic resins, dyes, pigments, and pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment
Use in industrial organic synthesis in manufacture of acetyl chloride, acid anhydrides, esters, nitriles, and diketene	Process enclosure; local exhaust ventilation; personal protective equipment
Use during laboratory operations as an acetylating agent	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of ketene, move the exposed person to fresh air at once. If breathing is difficult, properly trained personnel may assist the affected person by administering oxygen. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If ketene is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas.

- Waste disposal method:

Ketene may be disposed of by burning at a safe location or in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR KETENE

Condition	Minimum Respiratory Protection* Required Above 0.5 ppm
Vapor Concentration	
25 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 25 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR INORGANIC LEAD

INTRODUCTION

"Inorganic lead" is defined as lead oxides, metallic lead, and lead salts (including organic salts such as lead soaps but excluding lead arsenate). This guideline summarizes pertinent information about inorganic lead for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** Pb
- **Synonyms:** C.I. pigment metal 4, C.I. 77575, KS-4, lead flake, lead S2
- **Identifiers:** CAS 7439-92-1; RTECS OF7525000; DOT 1794
- **Appearance and odor:** Bluish-white, silvery, or gray odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 207.19
2. Boiling point (at 760 mmHg): 1,740 °C (3,164 °F)
3. Specific gravity (water = 1): 11.34
4. Melting point: 327.5 °C (621.5 °F)
5. Insoluble in water

- **Reactivity**

1. Incompatibilities: Lead reacts vigorously with oxidizing materials. Contact with hydrogen peroxide or active metals such as sodium or potassium may cause fires or explosions.
2. Hazardous decomposition products: Toxic fumes (e.g., lead oxide) may be released in a fire involving inorganic lead.

- **Flammability**

1. Extinguishant: Dry sand, dry dolomite, or dry graphite
2. Caution: Lead is combustible in powder form when exposed to heat or flame

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, inorganic lead should be treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for inorganic lead is 50 micrograms of lead per cubic meter of air ($\mu g/m^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift. If a worker is exposed to lead for more than 8 hours in any workday, the PEL, as a TWA for that day, shall be reduced according to the following formula: maximum permissible limit (in $\mu g/m^3$) = 400 divided by hours worked in the day. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 100 $\mu g/m^3$ as a TWA for up to a 10-hour workshift, 40-hr. workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.15 mg/m^3 (150 $\mu g/m^3$) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for inorganic lead

	Exposure units $\mu g/m^3$
OSHA PEL TWA	50
NIOSH REL TWA	100*
ACGIH TLV® TWA	150

* Air level to be maintained such that worker blood lead remains $\leq 60\ \mu g/100g$.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Inorganic lead may cause adverse health effects following exposure via inhalation or ingestion.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Summary of toxicology**

1. *Effects on animals:* In rats or mice, chronic oral administration or subcutaneous or intraperitoneal injection of lead subacetate, lead acetate, or lead phosphate produced cancer of the kidneys. Intravenous or intraperitoneal injection of lead nitrate, lead acetate, or lead chloride to pregnant mice, rats, or hamsters caused increased fetal mortality and malformations of the posterior extremities and urogenital and intestinal tracts in the offspring.
2. *Effects on humans:* Inhalation or ingestion of inorganic lead has caused peripheral neuropathy with paralysis of the muscles of the wrists and ankles, encephalopathy, anemia (due to decreased red blood cell life and impaired heme synthesis), proximal kidney tubule damage, decreased kidney function, and chronic kidney disease. Lead can accumulate in the soft tissues and bones, with the highest accumulation in the liver and kidneys, and elimination is slow. Lead can penetrate the placental barrier, resulting in neurologic disorders in infants.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to inorganic lead can cause decreased appetite, insomnia, headache, muscle and joint pain, colic, and constipation.
2. *Long-term (chronic):* Exposure to inorganic lead can cause weakness, weight loss, nausea, vomiting, constipation, blue or blue-black dot-like pigmentation on the gums ("lead line"), severe headache and abdominal cramps, delirium, convulsions, and coma.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to inorganic lead, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for t[illegible] anticipated occupational risks. These should concentrate [illegible] the function and integrity of the kidneys and the hematopoietic (blood cell forming), nervous, gastrointestinal, and reproductive systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to inorganic lead at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include preexisting neuromuscular disease. In addition to the medical interview and physical examination, the physician should consider obtaining additional baseline electrophysiologic and electromyographic studies and an assessment of fertility, using standardized methods and evaluation criteria. The physician should also obtain baseline values for the complete blood count including the reticulocyte count and for those tests which characterize prior internal exposure (e.g., blood lead level) and the effects of prior exposures (e.g., erythrocyte zinc protoporphyrin and delta-aminolevulinic acid dehydrogenase).

- **Periodic medical screening and/or biologic monitori[illegible]**

Occupational health interviews and physical examinati[illegible] should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to inorganic lead. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the kidneys and the hematopoietic (blood cell forming), nervous, gastrointestinal, and reproductive systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria: a complete blood count with reticulocyte count and those tests which characterize prior internal exposure (e.g., blood lead level) and the effects of exposures (e.g., erythrocyte zinc protoporphyrin and delta-aminolevulinic acid dehydrogenase).

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Becau[illegible] occupational exposure to inorganic lead may cause adve[illegible] reproductive effects and diseases of prolonged inductio[illegible] latency, the need for medical surveillance may extend well beyond termination of employment.

Sentinel health events

Acute SHE's include: Acute renal failure.

2. Delayed-onset or reproductive SHE's include: Inflammatory and toxic neuropathy and chronic renal failure.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to inorganic lead should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting inorganic lead with cellulose membrane filters followed by acid digestion and analysis by atomic absorption. A detailed sampling and analytical method for inorganic lead may be found in the *NIOSH Manual of Analytical Methods* (method number 7082).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum) and other appropriate protective clothing necessary to prevent skin contact with inorganic lead.

Workers should be provided with and required to use dust-proof safety goggles where inorganic lead may come in contact with the eyes.

SANITATION

Clothing which is contaminated with inorganic lead should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of inorganic lead from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of inorganic lead's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with inorganic lead should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle inorganic lead should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to inorganic lead may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for inorganic lead

Operations	Controls
During primary (ore) and secondary (scrap) smelting of lead; during the manufacture of storage batteries; during typecasting and remelting of type metal in printing	Process enclosure, local exhaust ventilation, dust control, personal protective equipment
During soldering in the fabrication of metal articles	Process enclosure, local exhaust ventilation, personal protective equipment
During melting and pouring of lead and alloys containing lead; during welding, burning, and cutting of metal structures containing lead or painted with lead containing surface coatings	Local exhaust ventilation, personal protective equipment
During the use of lead in the manufacture of surface coatings, including paints and varnishes; during the manufacture of ceramics and glass	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to inorganic lead, an eye-wash fountain should be provided within the immediate work area for emergency use.

If inorganic lead gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this compound.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to inorganic lead, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If inorganic lead gets on the skin, wash it immediately with soap and water. If inorganic lead penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If inorganic lead is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing inorganic lead, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing inorganic lead may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. If in solid form, inorganic lead may be collected and placed in an appropriate container.
6. Inorganic lead may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, an[illegible] cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for inorganic lead

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.5 mg/m³	Any supplied air respirator Any air-purifying respirator with a high-efficiency particulate filter Any self-contained breathing apparatus
Less than or equal to 1.25 mg/m³	Any powered air-purifying respirator with a high-efficiency particulate filter Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 2.5 mg/m³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 50 mg/m³	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Less than or equal to 100 mg/m³	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 100 mg/m³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 100 μg/m³ (TWA).

Occupational Health Guideline for Lindane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_6Cl_6$
- Synonyms: 1,2,3,4,5,6-Hexachlorocyclohexane; gamma-hexachlorocyclohexane; benzene hexachloride
- Appearance and odor: Colorless solid with a musty odor (pure material is odorless).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for lindane is 0.5 milligram of lindane per cubic meter of air (mg/m³) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Lindane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to lindane may cause vomiting, restlessness, muscle spasms, convulsions, and respiratory failure. It may also cause severe breathing difficulties which may be delayed in onset. Exposure to lindane vapors may cause headache, vomiting, and irritation of the eyes, nose, and throat. Repeated exposure to lindane may cause severe blood disorders which may be fatal. Skin rash may also occur from exposure to this chemical.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to lindane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to lindane at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders would be expected to be at increased risk from exposure. Examination of the eyes, central nervous system, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Lindane may cause aplastic anemia. A complete blood count should be performed, including a red cell count, a white cell count, and a differential count of a stained smear, as well as hemoglobin and hematocrit. The concentration of lindane in the blood is an indication of the extent of absorption.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Lindane (the gamma isomer of hexachlorocyclohexane) dust or vapor is a convulsant and causes cancer in mice. Repeated feeding to rats of 800 ppm in the diet resulted in mild liver damage; kidney damage occurred at higher levels. Mice fed 400 ppm in the diet developed liver tumors and, in some cases, lung metastases. In humans, accidental ingestion has caused fatalities; effects were repeated, violent, clonic convulsions, sometimes superimposed on a continuous tonic spasm; respiratory difficulty and cyanosis secondary to the convulsions were common. Exposure to the vapor causes irritation of the eyes, nose, and throat, severe headache, and nausea. Lindane levels in the blood do not appear to increase with increased duration of exposure but primarily reflect recent lindane absorption; production workers

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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exposed to air levels of 31 to 1800 ug/m^3 had blood levels of 1.9 to 8.3 ppb. Lindane has been suspected as a cause of aplastic anemia in a number of cases reported from various countries; this condition may have been caused either by a contaminant, or a thermal breakdown product of lindane, because many of the cases were associated with a space vaporizer as the source of exposure. The dry material applied to the skin of rabbits caused moderate skin irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 290.8
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.89
4. Vapor density (air = 1 at boiling point of lindane): Not applicable
5. Melting point: 112 C (234 F)
6. Vapor pressure at 20 C (68 F): 0.0000094 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.001
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Above 177 C (350 F) lindane decomposes to form toxic and irritating hydrogen chloride gas.
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving lindane.
4. Special precautions: None

- **Flammability**

1. Not combustible, but may be dissolved in a combustible solvent

- **Warning properties**

Since the vapor pressure is so low, warning properties are not considered.

Grant states that "as a dust, lindane is said to have caused irritation of the eyes and respiratory passages in particularly sensitive individuals. However, test applications of a 3% dust mixture with talc on the eyes and nasal mucosa of rabbits produced no irritation."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of lindane using a filter with subsequent recovery with iso-octane and gas chromatographic analysis. An analytical method for lindane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with lindane or liquids containing lindane where skin contact may occur.
- If employees' clothing may have become contaminated with lindane or liquids containing lindane, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with lindane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of lindane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the lindane, the person performing the operation should be informed of lindane's hazardous properties.
- Where exposure of an employee's body to lindane or liquids containing lindane may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with solid lindane should be removed promptly and non-impervious clothing which becomes contaminated with liquids containing lindane should be re-

moved immediately and not reworn until the lindane is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where lindane or liquids containing lindane may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquids containing lindane should be immediately washed or showered with soap or mild detergent and water to remove any lindane.
- Skin that becomes contaminated with solid lindane should be promptly washed or showered with soap or mild detergent and water to remove any lindane.
- Eating and smoking should not be permitted in areas where solid lindane is handled, processed, or stored.
- Employees who handle lindane or liquids containing lindane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to lindane may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of insecticides, scabicides, pediculicides, and vermifuges	Process enclosure; general dilution ventilation; personal protective equipment
Application as a pesticide on plant, animal, household, and agricultural premises and equipment	Personal protective equipment
Manufacture of lindane	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If lindane or liquids containing lindane get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If lindane or liquids containing lindane get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If lindane or liquids containing lindane soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of lindane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When lindane or liquids containing lindane have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If lindane is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing lindane should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Lindane may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

Lindane appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 5, 1974.

RESPIRATORY PROTECTION FOR LINDANE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m^3
Particulate Concentration	
5 mg/m^3 or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m^3 or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m^3 or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
1000 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 mg/m^3** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of lindane; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 1000 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Lithium Hydride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: LiH
- Synonyms: None
- Appearance and odor: Off-white, translucent solid which is odorless.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for lithium hydride is 0.025 milligram of lithium hydride per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Lithium hydride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Lithium hydride causes sneezing, coughing, and severe irritation of the nose and throat. Lithium hydride can cause severe eye and skin burns. If swallowed, the mouth, trachea, and esophagus may be burned. Inadvertent ingestion of lithium hydride may cause nausea, muscle twitches, mental confusion, blurring of vision, coma, and death.

2. Long-term Exposure: None reported. Nervous system damage has been reported from high short-term exposure.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to lithium hydride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to lithium hydride at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from lithium hydride exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of lithium hydride might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Lithium hydride is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Lithium hydride is a severe eye irritant and may cause tissue damage. Persons with pre-existing eye conditions may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Lithium hydride dust is a severe irritant of the eyes, respiratory tract, and skin due to the formation of lithium hydroxide and its caustic action on moist surfaces. The inherent toxicity of the lithium ion is high; a few milliequivalents in the plasma give rise to signs and symptoms of serious nervous system effects: anorexia, nausea, tremor, muscle twitches, apathy, mental confusion, blurring of vision, coma and death. Exposure of animals to concentrations of 5 to 55 mg/m^3 of lithium hydride caused sneezing and coughing; levels of 10 mg/m^3 corroded the body fur and skin of the legs, and there was occasionally severe inflammation of the eyes and nasal septum. Lesions of the nose and paws were similar to thermal burns and were attributed to the alkalinity of

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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the hydrolysis product of lithium hydride. The explosion of a cylinder of lithium hydride led to eye contact and swallowing of a small amount of the dust by a technician. The resulting burns caused scarring of both corneas, with strictures of the larynx, trachea, bronchi and esophagus; delayed death occurred. Exposure of humans to 0.5 mg/m^3 caused eye and skin irritation; 0.025 mg/m^3 caused sneezing, to which some degree of tolerance was acquired. Although unlikely to occur from industrial exposures, ingestion will cause severe burns of the mouth and esophagus. Restricted sodium intakes are reported to increase the toxicity of lithium.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 7.95
2. Boiling point (760 mm Hg): Decomposes at very high temperatures
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of lithium hydride): Not applicable
5. Melting point: 686 C (1267 F)
6. Vapor pressure at 20 C (68 F): 0 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts to form hydrogen gas and lithium caustic
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Moisture and carbon dioxide, even in concentrations normally in air; heat
2. Incompatibilities: Contact with oxidizers, halogenated hydrocarbons, and acids will cause fires and explosions. Contact with water will cause formation of flammable and explosive hydrogen gas. The heat of the reaction may be sufficient to cause ignition.
3. Hazardous decomposition products: Toxic gases and vapors (such as lithium hydride oxide) may be released in a fire involving lithium hydride.
4. Special precautions: Solid lithium hydride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 200 C (392 F) (may ignite spontaneously in moist air even at ambient temperatures)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Smother with nitrogen or other inert gas, or by covering containers, or cover with dry graphite or dry dolomite.

- **Warning properties**

According to Grant, "in rats, rabbits, and guinea pigs, it (lithium hydride dust) has been observed to cause irritation and inflammation in the eyes at concentrations which were very irritating to the respiratory tract." Grant states that even very low concentrations can produce respiratory irritation. According to the AIHA *Hygienic Guide*, "well-fitted respirators of the half mask type, when used with dust filters, protect adequately to 0.1 mg/m^3," because "persons with some degree of adaptation complain of eye and nose irritation at concentrations above 0.1 mg/m^3 . . . ."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for lithium hydride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with lithium hydride or liquids containing lithium hydride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with lithium hydride at or above an airborne concentration of 0.1 mg/m^3.

- If employees' clothing has had any possibility of being contaminated with lithium hydride or liquids containing lithium hydride, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with lithium hydride or liquids containing lithium hydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of lithium hydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the lithium hydride, the person performing the operation should be informed of lithium hydride's hazardous properties.
- Where there is any possibility of exposure of an employee's body to lithium hydride, liquids containing lithium or airborne concentrations of lithium hydride exceeding 0.5 mg/m^3, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with lithium hydride should be removed immediately and not reworn until the lithium hydride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of lithium hydride or liquids containing lithium hydride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to lithium hydride or liquids containing lithium hydride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with lithium hydride should be immediately brushed to remove any solid lithium hydride from the skin and washed or showered with copious quantities of water to remove any lithium hydride.
- Workers subject to skin contact with lithium hydride or liquids containing lithium hydride should wash any areas of the body which may have contacted lithium hydride at the end of each work day.
- Eating and smoking should not be permitted in areas where lithium hydride or liquids containing lithium hydride are handled, processed, or stored.
- Employees who handle lithium hydride or liquids containing lithium hydride should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to lithium hydride may occur and control methods which may be effective in each case:

Operation	Controls
Use in powder metallurgy; use in manufacture of buoyancy devices, fuel cells, and portable field generators; use in manufacture of reducing agent and propellant	General dilution ventilation; process enclosure; local exhaus ventilation; personal protective equipment
Use as a shielding material for thermal neutrons in nuclear industry; use as a desiccant; use as a condensing agent in organic synthesis; use in a condensation polymerization; use in manufacture of electronic tubes and in ceramics	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as an intermediate in manufacture of lithium aluminum hydride and lithium amide	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If lithium hydride or liquids containing lithium hydride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If lithium hydride or liquids containing lithium hydride get on the skin, immediately flush the contaminated skin with large amounts of water. If lithium hydride or liquids containing lithium hydride penetrate through the clothing, remove the clothing immediately and flush the skin with large amounts of water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of lithium hydride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If lithium hydride or liquids containing lithium hydride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the lithium hydride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If lithium hydride is spilled, the following steps should be taken:

1. Remove all igntion sources.
2. Ventilate area of spill.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Avoid contact with water.

- Waste disposal method:

Lithium hydride may be disposed of in dry sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Lithium Hydride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Spiegl, C. J., et al.: "Acute Inhalation Toxicity of Lithium Hydride," *A.M.A. Archives of Industrial Health*, 14:468-470, 1956.

RESPIRATORY PROTECTION FOR LITHIUM HYDRIDE

Condition	**Minimum Respiratory Protection* Required Above 0.025 mg/m³**
Particulate Concentration	
0.1 mg/m³ or less	Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
1.25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
50 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 50 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of lithium hydride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 50 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for LPG

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_3H_6 - C_3H_8 - C_4H_8 - C_4H_{10}$ mixture
- Synonyms: Liquefied petroleum gas; bottled gas
- Appearance and odor: Colorless, odorless gas (a foul-smelling odorant is usually added).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for LPG is 1000 parts of LPG per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of LPG per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

LPG can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to LPG can cause lightheadedness and drowsiness. Greater exposure may also cause unconsciousness and death. Contact with the liquid may also cause frostbite and irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to LPG.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to LPG at potentially hazardous levels.

- **Summary of toxicology**

LPG in gaseous form acts as a simple asphyxiant and a central nervous system depressant. In liquid form it may cause frostbite, as well as skin irritation. Toxicologic data are meager, and no chronic systemic effects have been reported from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 42— 58 depending on relative amounts of ingredients
2. Boiling point (760 mm Hg): −40 to −0.5 C (−40 to 31 F)
3. Specific gravity (water = 1): 0.5 to 0.58
4. Vapor density (air = 1 at boiling point of LPG): 1.6 to 2.0
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Propane: 8.6 atm.; Butane: 2.1 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving LPG.
4. Special precautions: LPG will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: 405 to 450 C (761 to 842 F)
3. Flammable limits in air, % by volume: Lower: 1.9; Upper: 9.5 (estimated)
4. Extinguishant: Stop flow of gas

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Warning properties**

1. Odor Threshold: Propane is the main constituent of LPG, according to the *Documentation of TLV's*. The odor threshold of propane (20,000 ppm) is 20 times the permissible exposure limit (1000 ppm).

2. Eye Irritation Level: Since propane is the main constituent of LPG, and since the eye irritation threshold of propane is above its lower flammable limit, eye irritation does not restrict respirator selection either for propane or for LPG

3. Evaluation of Warning Properties: The odor threshold of propane is 20 times higher than its permissible exposure limit. On the basis of the judgment that propane does not have adequate warning properties, for the purposes of this guideline, LPG is also assumed not to have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by utilizing a combustible gas meter. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure LPG may be used. An analytical method for LPG is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid LPG or from contact with vessels containing liquid LPG.
- Any clothing which becomes wet with liquid LPG should be removed immediately and not reworn until the LPG has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid LPG may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to LPG may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical industry as feedstock in catalytic cracking in manufacture of petrochemicals and polymers	Process enclosure; general dilution ventilation
Use as an internal combustion engine fuel	General dilution ventilation
Use in manufacture of synthetic rubber	Process enclosure; general dilution ventilation
Use as a fuel for industrial space and wall heating, air conditioning, and water heating	General dilution ventilation
Use as a fuel for drying agricultural products; use as a low sulfur fuel for cutting, soldering, and brazing	General dilution ventilation
Use as a fuel to augment public supply; to increase BTU content of manufactured gas	General dilution ventilation

Use as an aerosol propellant for shaving lather, window cleaners, starch sprays, room deoderants, insecticides, and pharmaceuticals	General dilution ventilation
Use as an agricultural tool in flame cultivation, non-selective cultivation, and weed control	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid LPG gets into the eyes, flush the eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Do not use hot water for eye flushing. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid LPG gets on the skin, immediately flush the contaminated skin with water. If liquid LPG soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of LPG, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If LPG is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

- Waste disposal method:

LPG may be disposed of by burning at a safe location or in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "LPG," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Underwriters' Laboratories: *LPG.*

RESPIRATORY PROTECTION FOR LPG

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
19,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 19,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Magnesium Oxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: MgO
- Synonyms: Magnesia fume
- Appearance: White fume.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for magnesium oxide fume is 15 milligrams of magnesium oxide fume per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for magnesium oxide fume a Threshold Limit Value of 10 mg/m³.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Magnesium oxide fume can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Magnesium oxide fume may cause irritation of the eyes and nose. It may also cause a metal fume fever. Symptoms of metal fume fever include chills, fever, headache, tightness of chest, cough, weakness, tiredness, dryness of the nose and mouth, muscular pain, nausea, and vomiting.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to magnesium oxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to magnesium oxide fume at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from magnesium oxide fume exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of magnesium oxide fume might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Magnesium oxide fume mildly irritates the eyes and nose. Examination of 95 workers exposed to an unspecified concentration of magnesium oxide dust revealed slight irritation of the eyes and nose; the magnesium level in the serum of 60% of those examined was above the normal upper limit of 3.5 mg%. Experimental subjects exposed to fresh magnesium oxide fume developed metal fume fever, an illness similar to influenza; their symptoms included fever, cough, oppression in the chest, and a leukocytosis. There are no reports of metal fume fever resulting from industrial exposure. Metal magnesium slivers produce a gaseous reaction and cause a slow-healing burn with ulceration, but this has not been reported for magnesium oxide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 40.3
2. Boiling point (760 mm Hg): 3582 C (6480 F) (solid)
3. Specific gravity (water = 1): Solid = 3.58
4. Vapor density (air = 1 at boiling point of magnesium oxide fume): Not applicable
5. Melting point: 2800 C (5072 F) (solid)

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6. Vapor pressure at 20 C (68 F): Essentially zero

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: Magnesium oxide fume reacts violently with chlorine trifluoride.

3. Hazardous decomposition products: None

4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Magnesium oxide fume may cause mild eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of magnesium oxide fume on a cellulose membrane filter, followed by treatment with nitric acid, and atomic absorption spectrophotometric analysis. An analytical method for magnesium oxide fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to magnesium oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fabrication of alloys for aircraft, ships, automobiles, boats, tools, machinery, and military equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from casting of metal and alloys	Local exhaust ventilation; general dilution ventilation
Liberation from fabrication of metal	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of magnesium oxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of magnesium oxide fume are inadvertently released, ventilate the area of release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Magnesium Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Magnesium," *Hygienic Guide Series*, Detroit, Michigan, 1960.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

RESPIRATORY PROTECTION FOR MAGNESIUM OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
150 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7,500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7,500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Malathion

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_{19}O_6PS_2$
- Synonyms: O,O-Dimethyl dithiophosphate of diethyl mercaptosuccinate; O,O-dimethyl S-(1,2-dicarbethoxyethyl) phosphorodithiocite
- Appearance and odor: Colorless to brown liquid with a mild skunk-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for malathion is 15 milligrams of malathion per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 15 mg/m^3 averaged over a work shift of up to ten hours per day, forty hours per week. The NIOSH Criteria Document for Malathion should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Malathion can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Malathion is one the least toxic of the organophosphate insecticides. Very large exposures are required to cause symptoms. After inhalation of malathion, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of the vision, tearing, runny nose, headache, and watering of the mouth. After swallowing malathion, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur, usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to the above symptoms, weakness, generalized twitching and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heartbeat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to malathion may make a person more susceptible to the effects of this and related chemicals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to malathion.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to malathion at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, liver, and attention to the cholinesterase levels in the blood should be stressed.

—Cholinesterase determination: Malathion can cause depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the erythrocytes should be measured by using medically acceptable biochemical tests before employment (or exposure) in order to establish an individual baseline

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value, which should be the mean of two ChE activity measurements, taken at least one day apart.

—14" x 17" chest roentgenogram: Malathion causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Malathion is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Malathion may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed quarterly or at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Malathion is a mild anticholinesterase agent; absorption may occur from inhalation of the mist, from skin absorption of solutions, or from ingestion. Malathion is less toxic to humans than most anticholinesterase agents because it is metabolized in the liver to an inactive form. However, ingestion of 50 to 90 cc of a 50% solution of malathion in a petroleum hydrocarbon base caused severe intoxication; the human LD50 is estimated to be about 1 g/kg. Signs and symptoms of intoxication by anticholinesterase agents are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nueromuscular system, and secretory glands. After inhalation of extremely high concentrations, respiratory and ocular effects may appear simultaneously. Respiratory effects include tightness in the chest, wheezing, laryngeal spasms, and excessive salivation. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear. Effects on the central nervous system may include giddiness, confusion, ataxia, and slurred speech. In a group of workers with maximum exposure of 56 mg/m^3 for 5 hours and an average of 3.3 mg/m^3, the cholinesterase levels in the blood were not significantly lowered and no one exhibited signs of cholinesterase inhibition. In a human experiment in which 4 men were exposed 1 hour daily for 42 days to 84.8 mg/m^3, there was moderate irritation of nose and conjunctiva but there were no cholinergic signs or symptoms.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 330
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.23
4. Vapor density (air = 1 at boiling point of malathion): Not applicable
5. Melting point: 2.8 C (37 F)
6. Vapor pressure at 20 C (68 F): 0.00004 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0145
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Starts to decompose at 49 C (140 F) but is not hazardous.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, phosphoric acid mist, and carbon monoxide) may be released in a fire involving malathion.
4. Special precautions: Malathion will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible.

- **Warning properties**

Since malathion has a negligible vapor pressure, warning properties are not considered.

Grant states that "undiluted technical liquid malathion dropped on a rabbits's eye caused slight immediate irritation with conjunctival hyperemia and edema of the lids, but the eye returned to normal in twenty-four hours."

The *Documentation of TLV's* notes that workers exposed to 84.8 mg/m^3 experienced moderate eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for malathion is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with malathion.
- Non-impervious clothing which becomes contaminated with malathion should be removed promptly and not reworn until the malathion is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid malathion may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to malathion, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with malathion should be promptly washed or showered with soap or mild detergent and water to remove any malathion.
- Employees who handle malathion should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where malathion is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to malathion may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticide products	Process enclosure; local exhaust ventilation; personal protective equipment
Application as an insecticide for treatment of grain, nut, fruit, and fiber crops; grasses, seeds, and tobacco; animals; agricultural premises	Personal protective equipment
Manufacture of malathion	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If malathion or formulations containing malathion get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If malathion or formulations containing malathion get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If malathion or formulations containing malathion penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of malathion, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When malathion or formulations containing malathion have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If malathion is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Malathion may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR MALATHION

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate or Vapor Concentration	
150 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
750 mg/m³ or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m³ or less	A powered chemical cartridge respirator with a full facepiece, helmet, or hood, an organic vapor cartridge, and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 5000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If an employee informs his employer that he is experiencing eye irritation from malathion while wearing a half- or quarter-mask respirator, the employer should provide an equivalent respirator with a full facepiece, helmet, or hood.

Occupational Health Guideline for Maleic Anhydride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CHCO)_2O$
- Synonyms: 2,5-Furanedione; cis-butenedioic anhydride; toxilic anhydride
- Appearance and odor: Colorless or white solid with a penetrating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for maleic anhydride is 0.25 part of maleic anhydride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1 milligram of maleic anhydride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Maleic anhydride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Maleic anhydride dust and vapor may cause irritation of the eyes, nose, throat, and skin. On contact with the skin, maleic anhydride may not cause an immediate burning sensation, especially if the skin is dry. If the solid form is allowed to remain in contact with moist tissues, burn may occur. Upon inhalation of dust or vapors, a person may experience coughing, sneezing, and burning of the throat. If the dust or vapors get into a person's eyes, irritation, sensitivity to light, and double vision may occur.

2. Long-term Exposure: Repeated or prolonged exposure to maleic anhydride may cause chronic skin or eye irritation. An allergic type of skin rash and asthma may also occur.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to maleic anhydride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to maleic anhydride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to maleic anhydride would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Maleic anhydride in the form of a vapor, fume, or dust is a severe irritant of the eyes; it is both an irritant and sensitizer of both the skin and respiratory tract, and may produce asthma on repeated exposures. In a carcinogenesis experiment with a few rats injected subcutaneously with 1 mg maleic anhydride in oil twice weekly for 61 weeks, 2 of 3 surviving animals developed fibrosarcomas which appeared 80 weeks after the start of the experiment. Workers exposed to vapors from heated maleic anhydride developed an intense burning sensation in the eyes and throat, with cough and vomiting; exposure to high fume concentrations caused photophobia, double vision, and a sensation of seeing rings around lights. Exposure of humans to a concentration of

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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6 to 8 mg/m^3 of air resulted in nasal irritation within 1 minute and eye irritation after 15 to 20 minutes. Among workers repeatedly exposed to 5 to 10 mg/m^3 there was ulceration of nasal mucous membranes, chronic bronchitis, and some asthma. The dust on dry skin may result in a delayed burning sensation, but on moist skin the sensation is almost immediate, producing erythema which may progress to vesiculation. Prolonged or repeated exposure also may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.1
2. Boiling point (760 mm Hg): 202 C (396 F)
3. Specific gravity (water = 1): 1.43 (solid); 1.3 (melt)
4. Vapor density (air = 1 at boiling point of maleic anhydride): 3.38
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): 0.16 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble but reacts slowly and dissolves
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Maleic anhydride is decomposed by water at temperatures above 66 C (150 F).
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with alkali metals, caustics, and amines may cause polymerization if temperature is greater than 66 C (150 F).
3. Hazardous decomposition products: Toxic gases and vapors (such as irritating fume of unburned material and carbon monoxide) may be released in a fire involving maleic anhydride.
4. Special precautions: None

- **Flammability**

1. Flash point: 102 C (215 F) (closed cup)
2. Autoignition temperature: 477 C (890 F)
3. Flammable limits in air, % by volume: Lower: 3.4 (calculated); Upper: 7.1
4. Extinguishant: Alcohol foam, carbon dioxide. Dry chemical, multi-purpose dry chemical, or loaded stream fire extinguishing media should not be used because of the possibility of an explosion due to the probable reaction of basic compounds in these extinguishing media with maleic anhydride.

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, "at a concentration of 2 mg/m^3 a faint odor is noticed."
2. Eye Irritation Level: Exposure to a concentration of 6 to 8 mg/m^3 maleic anhydride results in eye irritation within 15 to 20 minutes, according to the *Hygienic Guide*, which also states that "a tendency for eye irritation at levels of approximately 1 mg/m^3 has been observed."

Grant reports that maleic anhydride is a "crystalline material which powders and sublimes readily, producing fumes which are powerfully irritating to the eyes and respiratory tract." Grant gives no quantitative information, however.

3. Other Information: The *Hygienic Guide* notes that at a concentration of 6 to 8 mg/m^3 "persons not accustomed to handling maleic anhydride report definite nasal irritation within 1 minute."
4. Evaluation of Warning Properties: Through its odor maleic anhydride can be detected at a concentration of only twice the TLV. In addition, the *Hygienic Guide* states that eye irritation can occur at the TLV.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for maleic anhydride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid maleic anhydride or liquids containing maleic anhydride.

- Clothing contaminated with maleic anhydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of maleic anhydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the maleic anhydride, the person performing the operation should be informed of maleic anhydride's hazardous properties.
- Non-impervious clothing which becomes contaminated with maleic anhydride should be removed promptly and not reworn until the maleic anhydride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid maleic anhydride or liquids containing maleic anhydride contacting the eyes.
- Where there is any possibility of exposure of an employee's body to solid or liquid maleic anhydride or liquids containing maleic anhydride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid maleic anhydride or liquids containing maleic anhydride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with maleic anhydride should be promptly washed or showered with soap or mild detergent and water to remove any maleic anhydride.
- Employees who handle solid or liquid maleic anhydride or liquids containing maleic anhydride should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to maleic anhydride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of polyester resins for automobile bodies, structural building panels, molded boats, and chemical storage tanks	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of fumaric acid (as food acidulant) and polyester; use in manufacture of alkyld resins as enamels, interior flat finishes, automotive finishes, printing inks, reactive plasticizers, and marine paints and varnishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of detergents and lubricating additives as dispersant and wetting agent; use in manufacture of drying oils	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of tall oil resins as general coating and industrial dip cotaing; use in manufacture of terpene resins as shellac substitutes, in aniline inks, as protective coatings on paper, in metal foil, cellulose films, and natural and synthetic fiber	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of chlorendic anhydride for fire-retardant polyester resins, as expoxy hardener, component of military paints, manufacture of extreme pressure lubricants; and use in organic synthesis and in production of chemical intermediates	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If maleic anhydride gets into the eyes, wash eyes immediately with copious amounts of water, lifting the lower and upper lids occasionally. If irritation or other eye problems are present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If maleic anhydride gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If maleic anhydride or liquids containing maleic anhydride penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of maleic anhydride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When maleic anhydride has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If maleic anhydride is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. Large quantities should be collected in the most convenient and safe manner for reclamation or disposal in a secured sanitary landfill.

- Waste disposal methods:

Maleic anhydride may be disposed of:

1. By making packages of maleic anhydride in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving maleic anhydride in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By placing maleic anhydride in closed containers and depositing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR MALEIC ANHYDRIDE

Condition	Minimum Respiratory Protection* Required Above 0.25 ppm
Particulate or Vapor Concentration	
12.5 ppm or 50 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 ppm or 1000 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and a high efficiency particulate filter and a full facepiece, helmet, or hood.
500 ppm or 2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 500 ppm or 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Manganese

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Mn
- Synonyms: None
- Appearance: Gray solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for manganese is a ceiling level of 5 milligrams of manganese per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Manganese can affect the body if it is inhaled. Manganese can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of fumes with high concentrations of manganese and its oxides may bring about "metal fume fever." Symptoms of metal fume fever are chills and fever, upset stomach, vomiting, dryness of the throat, cough, weakness, and aching of the head and body. Symptoms often occur several hours after exposure to fumes and usually last for only a day.

2. Long-term Exposure: Prolonged or repeated exposure to manganese may affect the nervous system with difficulty in walking and balancing, weakness or cramps in the legs, hoarseness of the voice, trouble with memory and judgment, unstable emotions or unusual irritability. If high exposure continues, a person may have poor coordination, difficulty in speaking clearly, or shaking or tremor of the arms or legs. A person may also have hallucinations or uncontrollable laughter or crying. The respiratory system may be affected by a condition known as "manganese pneumonia," which may result in symptoms and signs of coughing, fever, chills, general aching of the body, chest pain, and other common signs of pneumonia.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to manganese.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to manganese at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of alcoholism, psychiatric, neurologic, or pulmonary diseases or liver dysfunction would be expected to be at increased risk from exposure. Examination of the respiratory tract, hemopoietic system, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Manganese causes pneumonitis or metal fume fever. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Manganese is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

—A complete blood count: Manganese has been reported to cause blood changes. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage has been observed in humans exposed to manganese, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged

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sediment. Determination of manganese level in urine may be helpful in assessing exposure.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Inhalation of manganese dust or fume primarily affects the central nervous system; high concentrations cause the influenza-like illness termed manganese pneumonitis. Manganese acts either as a direct neurotoxin, or it adversely affects certain neuroenzymes. Manganese fume causes a disease quite similar to Parkinsonism after 6 months to 2 years of exposure. Initially there is headache; asthenia; restless sleep or somnolence; change in personality with psychomotor instability associated with restlessness, irritability, and a tendency to either cry or laugh inappropriately. This is followed by an intermediate phase with visual hallucinations, double vision; impaired hearing; uncontrollable impulses; mental confusion; euphoria; and normal reaction to painful stimuli. In the advanced phase, the subject exhibits possible anemia; excessive salivation; disorders of the basal ganglia of Parkinsonian type, such as mask-like facies, muscle weakness, muscle rigidity, tremor of the uppper extremities and head, and impaired gait. High concentrations of manganese dust produce fever and chills similiar to mental fume fever. During human exposure to manganese fume there is dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness, constriction in the chest, and a dry cough. Several hours following exposure the subject develops chills, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting. Physical examination reveals fever, perspiration, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity. Leukopenia has been reported in 4 out of 16 cases of manganese poisoning, although there is no convincing evidence that any changes in the blood should be regarded as specific or diagnostic of manganism.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 54.94
2. Boiling point (760 mm Hg): 2097 C (3806 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of manganese): Data not available
5. Melting point: 1245 C (2273 F)
6. Vapor pressure at 1227 C (2240 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Not pertinent
8. Evaporation rate (butyl acetate = 1): Not pertinent

2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Data not available

- **Warning properties**

Grant states that "local contact of manganese with the cornea does not appear to be a problem industrially."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of manganese. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of manganese in a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for manganese is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to manganese may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during welding operations	Local exhaust ventilation; respiratory protective devices; dilution ventilation
Liberation during casting of molten ferro-manganese	Local exhaust ventilation
Liberating during bagging of manganese ore	Local exhaust ventilation; respiratory protective devices and dust suppression with water
Liberation during mixing and pressing of dry battery depolarization	Local exhaust ventilation
Liberation during grinding of ore containing manganese	Local exhaust ventilation; respiratory protective devices and dust suppression with water
Liberation during arc burning of manganese-hardened steel in repair and manufacture programs	Local exhaust ventilation; respiratory protective devices; dilution ventilation
Liberation from top of submerged arc electric furnace	General dilution ventilation and process enclosure, if possible
Liberation of dust during ore extraction	General dilution ventilation; respiratory protective devices
Liberation during metal finishing operations of high manganese steel	Local exhaust ventilation; respiratory protective equipment
Liberation of dust during crushing of ferro-manganese mètal prior to shipment; during dumping, weighing, and mixing operations in ceramics and glass manufacture for pigmentation and coloration purposes	Local exhaust ventilation; respiratory protective equipment
Liberation from formulation of proprietary mixtures for paint and varnish manufacture	Local exhaust ventilation; respiratory protective equipment
Liberation of dioxide and sulfate during manufacture and application of fertilizers	Local exhaust ventilation
Liberation of dust during manufacture of manganese soap and wood preservatives; manufacture of safety matches, signal flares, fire-works, and strikers; during mixing and kiln operations of brick manufacture	Local exhaust ventilation
Liberation of dusts during manufacture and utilization of oxidation catalysts, such as hopcalite, manganese acetate, and naphthenate	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of manganese, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When manganese has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If manganese is spilled, the following steps should be taken:

1. Remove all ignition sources.

2. Ventilate area of spill.

2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Manganese may be disposed of:

1. By making packages of manganese in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving manganese in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on manganese, look up manganese in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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RESPIRATORY PROTECTION FOR MANGANESE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m^3
Dust or Mist Concentration	
25 mg/m^3 or less	Any dust and mist respirator, except single-use respirators.
50 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
50 mg/m^3 or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
10,000 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Inorganic Mercury

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Hg
- Synonyms: Quicksilver
- Appearance and odor: Silvery, mobile, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mercury is a ceiling level of 0.1 milligram of mercury per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 0.05 mg/m^3 averaged over an eight-hour work shift. The NIOSH Criteria Document for Inorganic Mercury should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mercury can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhaled mercury vapor may cause headaches, cough, chest pains, chest tightness, and difficulty in breathing. It may also cause chemical pneumanitis. In addition, it may cause soreness of the mouth, loss of teeth, nausea, and diarrhea. Liquid mercury may irritate the skin.

2. Long-term Exposure: Repeated or prolonged exposure to mercury liquid or vapor causes effects which develop gradually. The first effects to occur are often fine shaking of the hands, eyelids, lips, tongue, or jaw. Other effects are allergic skin rash, headache, sores in the mouth, sore and swollen gums, loose teeth, insomnia, excess salivation, personality change, irritability, indecision, loss of memory, and intellectual deterioration.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to mercury.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to mercury at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of allergies or known sensitization to mercury, chronic respiratory disease, nervous system disorders, or kidney disease would be expected to be at increased risk from exposure. Examination for any signs or symptoms of unacceptable mercury absorption such as weight loss, insomnia, tremors, personality changes, or other evidence of central nervous system involvement, as well as evidence of kidney damage, should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to mercury, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Determination of mercury level in urine may be helpful in assessing extent of absorption.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Summary of toxicology**

Acute exposure to mercury at high levels causes severe respiratory irritation, digestive disturbances, and marked renal damage; chronic mercurialism, the form of intoxication most frequently caused by occupational exposure, is characterized by neurologic and psychic disturbances, anorexia, weight loss, and stomatitis. Skin absorption of inorganic mercury probably adds to the toxic effects of vapor inhalation. Intraperitoneal injection of metallic mercury in rats has produced sarcomas. Exposure of humans to mercury vapor in concentrations of 1.2 to 8.5 mg/m^3 causes cough, chest pain and dyspnea, leading to bronchitis and pneumonitis. Metallic mercury readily vaporizes at room temperature, and the vapor has no warning properties. At low levels, the onset of symptoms resulting from chronic exposure is insidious; fine tremors of the hands, eyelids, lips and tongue are often the presenting complaint. Coarse jerky movements and incoordination may interfere with the fine movements considered necessary for writing and eating. Psychic disturbances such as insomnia, irritability, and indecision occur; headache, excessive fatigue, anorexia, digestive disturbances, and weight loss are common; stomatitis with excessive salivation is sometimes severe; muscle weakness has been reported. Proteinuria may occur, but is relatively infrequent. Mercury has been reported to be capable of causing sensitization dermatitis. Examination of urine for mercury may be of value. There is no "critical" level of mercury in urine above or below which poisoning cannot be seen. Various observers have suggested from 0.1 to 0.5 mg of Hg/l of urine as having clinical significance. Mercury, particularly organic forms, is known to adversely affect the fetus if the mother is exposed during pregnancy.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 200.6
  2. Boiling point (760 mm Hg): 357 C (674 F)
  3. Specific gravity (water = 1): 13.5
  4. Vapor density (air = 1 at boiling point of mercury): Not applicable
  5. Melting point: −39 C (-38 F)
  6. Vapor pressure at 20 C (68 F): 0.0012 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.002
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with acetylene, acetylene products, or ammonia gases may form solid products that are sensitive to shock and which can initiate fires of combustible materials.
  3. Hazardous decomposition products: None
  4. Special precautions: Mercury can attack copper and copper alloy materials.
- **Flammability**
  1. Not combustible
- **Warning properties**
  1. Odor Threshold: Mercury is odorless.
  2. Eye Irritation Level: Grant states that "when mercury metal droplets are in the epithelium, rather than the corneal stroma or anterior chamber, they are extruded rapidly with little reaction, as was reported in a patient who was sprayed forcefully with metallic mercury and was observed to have many fine silvery globules beneath the epithelium of the cornea . . . .

"Mercury metal in contact with the conjunctiva has been shown in rabbits to be absorbed and ultimately to be detectable in the urine. While in contact with the conjunctiva, metallic mercury produced no clinical signs of conjunctivitis, but histologically an inflammatory reaction has been demonstrable. External contact with mercury vapor has repeatedly been observed to induce a characteristic discoloration of the crystalline lens (mercurialentis)." Mercurialentis also is caused by systemic poisoning "from absorption of mercury vapor through the respiratory tract, the skin, and the gastrointestinal tract."

For the purposes of this guideline, mercury is not treated as an eye irritant.

3. Evaluation of Warning Properties: Mercury has no warning properties, according to the *Hygienic Guide*.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of mercury. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of mercury with a three-section solid phase sampler, followed by analysis with an atomic absorption spectrophotometer. An analytical method for mercury is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may

be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid mercury.
- If employees' clothing may have become contaminated with mercury, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with mercury should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of mercury from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the mercury, the person performing the operation should be informed of mercury's hazardous properties.
- Non-impervious clothing which becomes contaminated with mercury should be removed promptly and not reworn until the mercury is removed from the clothing.

SANITATION

- Workers subject to skin contact with liquid mercury should wash with soap or mild detergent and water any areas of the body which may have contacted mercury at the end of each work day.
- Skin that becomes contaminated with mercury should be promptly washed or showered with soap or mild detergent and water to remove any mercury.
- Eating and smoking should not be permitted in areas where mercury is handled, processed, or stored.
- Employees who handle mercury should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to mercury may occur and control methods which may be effective in each case:

Operation	Controls
Use as a liquid cathode in electrolytic production of chlorine and caustic soda from brine	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use during manufacture and repair of industrial and medical apparatus; use during manufacture of inorganic and organic compounds for use as pesticides, antiseptics, germicides, and skin preparations, and miscellaneous applications as chemical intermediates, preservatives, and pigments	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use in preparation of amalgams for use in tooth restorations, chemical processing, and molding operations; use during manufacture of mildew-proof paints and marine antifouling agents	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of organic mercurials; use in manufacture of batteries, lamps, and power tubes; manufacture of tungsten-molybdenum wire and rods; use in manufacture of inorganic salts for use as catalysts in production of urethanes, vinyl chloride monomers, anthraquinone derivatives, and other miscellaneous chemicals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

Operation	Controls
Use as a chemical intermediate and in the manufacture of felt; as a flotation agent in manufacture of bowling balls; use as a laboratory reagent or as a working fluid in instruments	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use as a conductor during construction and maintenance of military and nuclear power systems, in mercury-stem boilers, and in air-rectifiers	General dilution ventilation; personal protective equipment; meticulous housekeeping
Liberation during roasting and smelting operations	General dilution ventilation; local exhaust ventilation
Use in manufacture of explosives; in preparation of amalgams for use in artificial jewelry	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use in manufacture of compounds for pulp and paper industry as controls for biological growths	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during mining and subsequent refining of ore containing cinnabar	General dilution ventilation; personal protective equipment; meticulous housekeeping

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid mercury gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid mercury gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid mercury penetrates through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of mercury, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When large quantities of mercury have been swallowed or mercury has been swallowed repeatedly and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If mercury is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material for reclamation using commercially available mercury vapor depressants or specialized vacuum cleaners.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Mercury as Hg," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR INORGANIC MERCURY

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m^3**
Particulate or Vapor Concentration	
1 mg/m^3 or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
28 mg/m^3 or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 28 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against mercury. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Organo (Alkyl) Mercury

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all organo (alkyl) mercury compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Ethylmercuric chloride

- Formula: C_2H_5HgCl
- Synonyms: Chloroethylmercury; ceresan
- Appearance and odor: Colorless, odorless solid.

Dimethylmercury

- Formula: $(CH_3)_2Hg$
- Synonyms: Mercury dimethyl
- Appearance and odor: Colorless liquid with a weak, sweetish odor.

Diethylmercury

- Formula: $(C_2H_5)_2Hg$
- Synonyms: Mercury diethyl
- Appearance and odor: Colorless liquid with a weak, sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for organo (alkyl) mercury is 0.01 milligram of organo (alkyl) mercury per cubic meter of air (mg/m^3) averaged over an eight-hour work shift, with a ceiling level of 0.04 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Organo (alkyl) mercury can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Organo (alkyl) mercury compounds may cause damage to the central nervous system and are irritants of the eyes, respiratory tract, and skin. Symptoms of methyl and ethyl mercury intoxication may occur weeks to months after an acute exposure to toxic concentrations. The symptoms of acute and chronic intoxication from both compounds are similar and include numbness and tingling of the lips, hands and feet, staggering, joint pain, narrowing of vision, hearing difficulties, and emotional disturbances. With severe intoxication the symptoms are usually irreversible. Severe intoxication also results in periods of spasticity and jerking movements of the arms and legs, head or shoulders, and bouts of groaning, moaning, shouting, or crying. Other symptoms are dizziness, increased watering of the mouth, watering of the eyes, nausea, vomiting, and diarrhea or constipation. Infants born to mothers who have been exposed to large amounts of methyl mercury have shown mental retardation and cerebral palsy with convulsions. The symptoms of exposure to methoxyethyl mercury are loss of appetite, diarrhea, weight loss, and fatigue. Kidney damage has occurred. The alkyl mercury halides are irritating to the eyes, upper respiratory tract, and skin and may cause severe skin rash and burns. Allergic skin rashes may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to organo (alkyl) mercury.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to organo (alkyl) mercury at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, the kidneys, and eyes should be stressed. The skin should be examined for evidence of chronic disorders.

—Blood test: Analysis of the blood for mercury may be useful in monitoring absorption.

—Urinalysis: Since kidney damage has been observed in humans exposed to organo mercury, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Organo (alkyl) mercury compounds cause dysfunction of the central nervous system and irritate the eyes, mucous membranes, and and skin. Symptoms of methyl and ethyl mercury intoxication may occur weeks to months after an acute exposure to toxic concentrations. The symptoms of acute and chronic intoxication from both compounds are similar and include numbness and tingling of the lips, hands, and feet; ataxia; dysarthria; concentric constriction of the visual fields (tunnel vision); impairment of hearing; and emotional disturbances. With severe intoxication, the symptoms are usually irreversible. Severe intoxication also results in incontinence, periods of spasticity and jerking movements of the limbs, head or shoulders, and bouts of groaning, moaning, shouting, or crying; less frequent symptoms are dizziness, hypersalivation, lacrimation, nausea, vomiting, and diarrhea or constipation. An epidemic of intoxication from ingestion of fish contaminated with methyl mercury occurred in the Minamata district in Japan, and methyl mercury intoxication is often referred to as Minamata disease. Infants born to mothers with exposure to large amounts of methyl mercury had mental retardation and cerebral palsy with convulsions; methyl mercury has a strong effect on cell division and chromosome segregation, which may produce chromosomal alterations. The biological half-life in humans for methyl mercury is about 70 days; since elimination is slow, irregular, and individualized, there is a considerable risk of an accumulation of mercury to toxic levels. A precise relationship between atmospheric levels and concentrations of mercury in blood or urine cannot be shown. Clinical observations indicate that concentrations of 50 to 100 ug mercury/100 ml of whole blood may be associated with symptoms of intoxication; concentrations around 10 to 20 ug mercury/100 ml are not associated with symptoms. In a study of 20 workers engaged in the manufacture of organic mercurials and exposed for 6 years to mercury concentrations in air between 0.01 and 0.1 mg/m^3, there was no evidence of physical impairment or clinical laboratory abnormalities. The symptoms of exposure to methoxyethyl mercury are anorexia, diarrhea, weight loss, and fatigue, and are probably due to inorganic mercury; kidney damage with albuminuria, and occasionally a nephrotic syndrome, has occurred. The alkyl mercury halides are irritating to the eyes, mucous membranes, and skin and may cause severe dermatitis and burns; skin sensitization has occasionally occurred.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Ethylmercuric chloride**

1. Molecular weight: 265.1
2. Boiling point (760 mm Hg): Sublimes above 40 C (104 F)
3. Specific gravity (water = 1): 3.48
4. Vapor density (air = 1 at boiling point of ethylmercuric chloride): 9.2
5. Melting point: 192 C (378 F)
6. Vapor pressure at 20 C (68 F): Much less than 1
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00014
8. Evaporation rate (butyl acetate = 1): Data not available

- **Physical data—Dimethylmercury**

1. Molecular weight: 230.7
2. Boiling point (760 mm Hg): 95 C (203 F)
3. Specific gravity (water = 1): 3.2
4. Vapor density (air = 1 at boiling point of dimethylmercury): 7.9
5. Melting point: −80 C (−112 F) (approximately)
6. Vapor pressure at 20 C (68 F): 50 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Physical data—Diethylmercury**

1. Molecular weight: 258.7
2. Boiling point (760 mm Hg): 159 C (318 F)
3. Specific gravity (water = 1): 2.5
4. Vapor density (air = 1 at boiling point of diethylmercury): 8.9
5. Melting point: Data not available (very low)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures cause decomposition to flammable and explosive hydrocarbon gases.
2. Incompatibilities: Contact with strong oxidizers such as chlorine may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases

and vapors (such as toxic mercury fumes and carbon monoxide) may be released in a fire involving organo (alkyl) mercury.

4. Special precautions: Liquid organo (alkyl) mercury will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Ethylmercuric chloride: Not applicable; Dimethylmercury and diethylmercury: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The American National Standards Institute (ANSI) states that many alkyl mercury compounds "are disagreeable in odor."

2. Irritation Levels: ANSI states that "the organomercurials are severe skin, eye, and mucous membrane irritants. The first complaints following surface contact may be delayed for several hours and are usually those of local warmth and redness, which progress to blistering. In cases of repeated exposure, skin sensitization may occur."

3. Evaluation of Warning Properties: Not all alkyl mercury compounds have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of organo (alkyl) mercury. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

An analytical method for organo (alkyl) mercury is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with organo (alkyl) mercury or liquids containing organo (alkyl) mercury.
- If employees' clothing has had any possibility of being contaminated with organo (alkyl) mercury or liquids containing organo (alkyl) mercury, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with organo (alkyl) mercury should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of organo (alkyl) mercury from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the organo (alkyl) mercury, the person performing the operation should be informed of organo (alkyl) mercury's hazardous properties.
- Where there is any possibility of exposure of an employee's body to organo (alkyl) mercury or liquids containing organo (alkyl) mercury, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with organo (alkyl) mercury should be removed immediately and not reworn until the organo (alkyl) mercury is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of organo (alkyl) mercury or liquids

containing organo (alkyl) mercury contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to organo (alkyl) mercury or liquids containing organo (alkyl) mercury, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with organo (alkyl) mercury should be immediately washed or showered with soap or mild detergent and water to remove any organo (alkyl) mercury.
- Workers subject to skin contact with organo (alkyl) mercury or liquids containing organo (alkyl) mercury should wash with soap or mild detergent and water any areas of the body which may have contacted organo (alkyl) mercury at the end of each work day.
- Eating and smoking should not be permitted in areas where organo (alkyl) mercury or liquids containing organo (alkyl) mercury are handled, processed, or stored.
- Employees who handle organo (alkyl) mercury or liquids containing organo (alkyl) mercury should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to organo (alkyl) mercury may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture/production for use as fungicides and slimicides	Replacement/substitution; dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during processing mercury ore and during mining and extraction operations	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in treating and disinfecting of seeds and bulbs	Replacement/substitution; general dilution ventilation; personal protective equipment
Liberation during utilization (spraying) of seeds and bulbs	Replacement/substitution; general dilution ventilation; personal protective equipment
Use as a wood, timber, and paper preservative and slimicide; liberation during analysis at seed control stations	Replacement/substitution; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If organo (alkyl) mercury or solutions containing organo (alkyl) mercury compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solid organo (alkyl) mercury or solutions containing organo (alkyl) mercury get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solid organo (alkyl) mercury or solutions containing organo (alkyl) mercury penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention.

- **Breathing**

If a person breathes in large amounts of organo (alkyl) mercury, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When organo (alkyl) mercury has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If organo (alkyl) mercury compounds are spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the solid form, collect for reclamation or disposal in sealed containers in a secured sanitary landfill.
4. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and reclaimed or collected for reclamation or disposal in sealed containers in a secured sanitary landfill.

- Waste disposal methods:

Organo (alkyl) mercury may be disposed of:
1. If in the solid form, by collecting for reclamation or for disposal in sealed containers in a secured sanitary landfill.
2. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and reclaimed or collected for reclamation or disposal in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ORGANO (ALKYL) MERCURY

Condition	**Minimum Respiratory Protection*** **Required Above 0.01 mg/m³**
Particulate or Vapor Concentration	
0.5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 10 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organo (alkyl) mercury vapors and particulates. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of organo (alkyl) mercury; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

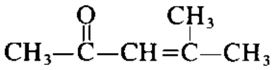
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR MESITYL OXIDE

INTRODUCTION

This guideline summarizes pertinent information about mesityl oxide for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{10}O$
- **Structure:**



$$CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$$

- **Synonyms:** Isobutenyl methyl ketone, isopropylidene acetone, methyl isobutenyl ketone, 4-methyl-3-penten-2-one
- **Identifiers:** CAS 141-79-7; RTECS SB4200000; DOT 1229, label required: "Flammable Liquid"
- **Appearance and odor:** Oily, colorless or pale yellow liquid with a strong odor like peppermint

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.16
2. Boiling point (at 760 mmHg): 130°C (266°F)
3. Specific gravity (water = 1): 0.856
4. Vapor density (air = 1 at boiling point of mesityl oxide): 3.4
5. Melting point: -46°C (-50.8°F)
6. Vapor pressure at 20°C (68°F): 8 mmHg; at 25°C (77°F), 9.5 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 3
8. Evaporation rate (butyl acetate = 1): 0.85
9. Saturation concentration in air (approximate): At 20°C (68°F), 1.05% (10,500 ppm); at 25°C (77°F), 1.25% (12,500 ppm)
10. Ionization potential: 9.08 eV

- **Reactivity**

1. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving mesityl oxide.
3. Caution: Mesityl oxide may dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 30.6°C (87°F) (closed cup)
2. Autoignition temperature: 344°C (652°F)
3. Flammable limits in air, % by volume: Lower, 1.3; upper, 8.8
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 0.45 ppm
2. Eye irritation level: 25 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, mesityl oxide can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for mesityl oxide is 25 parts of mesityl oxide per million parts of air (ppm) [100 milligrams of mesityl oxide per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 10 ppm (40 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 15 ppm (60 mg/m^3) as a TWA for a normal 8-hour workday or a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 25 ppm (100 mg/m^3) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for mesityl oxide

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	25	100
NIOSH REL TWA	10	40
ACGIH TLV® TWA	15	60
STEL	25	100

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mesityl oxide may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of mesityl oxide by mice or rabbits produced narcosis, tissue destruction (necrosis) of the liver, hemorrhage and edema of the lungs, alimentary tract distention, and death. Subchronic inhalation of mesityl oxide by rats, mice, or guinea pigs caused congestion of the liver and lungs and damage to the kidney tubules.
2. *Effects on humans:* Exposure of workers to mesityl oxide has caused centeral nervous system depression and narcosis.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to mesityl oxide can cause headache, dizziness, breathing difficulty (dyspnea), and unconsciousness. Irritation of the eyes, nose, and throat can also occur.
2. *Long-term (chronic):* Exposure to mesityl oxide can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to mesityl oxide, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to mesityl oxide at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to mesityl oxide. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to mesityl oxide should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting mesityl oxide vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure mesityl oxide may also be used. A detailed sampling and analytical method for mesityl oxide may be found in the *NIOSH Manual of Analytical Methods* (method number 1301).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with mesityl oxide.

Workers should be provided with and required to use splash-proof safety goggles where mesityl oxide may come in contact with the eyes.

SANITATION

Clothing which is contaminated with mesityl oxide should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of mesityl oxide from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of mesityl oxide's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with mesityl oxide should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle mesityl oxide should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to mesityl oxide may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for mesityl oxide

Operations	Controls
During spray application of lacquers and stains; during use as a solvent	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a paint and varnish remover and carburetor cleaner	General dilution ventilation, personal protective equipment
During preparation and application of roll-coating inks	Process enclosure, local exhaust ventilation, personal protective equipment
During flotation processes for selective benefaction of ores	Natural ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to mesityl oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

If mesityl oxide gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to mesityl oxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If mesityl oxide gets on the skin, wash it immediately with soap and water. If mesityl oxide penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If mesityl oxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing mesityl oxide, absorb on paper towels and place in appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from mesityl oxide vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing mesityl oxide may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Mesityl oxide should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing mesityl oxide may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for mesityl oxide

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 500 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed) Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 5,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 5,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 10 ppm (40 mg/m^3) (TWA).

Occupational Health Guideline for Methoxychlor

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{16}H_{15}Cl_3O_2$
- Synonyms: 2,2-Bis(p-methoxyphenyl)-1,1,1-trichloroethane
- Appearance and odor: Colorless to tan solid with a slight fruity odor (or emulsifiable solution in heavy aromatic naphtha).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methoxychlor is 15 milligrams of methoxychlor per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for methoxychlor a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methoxychlor can affect the body if it is inhaled. It can also affect the body if it is swallowed.

- **Effects of overexposure**

There are no reported effects in humans from exposure to methoxychlor. Animal experiments have shown that this chemical may produce trembling, convulsions, and mild kidney and liver damage. Women may be at increased risk.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methoxychlor.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methoxychlor at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methoxychlor exposure.

—Liver disease: Methoxychlor causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Methoxychlor causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Convulsive and other neurologic disorders: Methoxychlor causes convulsions and other neurologic disorders in animals. Persons with a history of such disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methoxychlor affects the nervous system and causes convulsions in animals. The oral LD50 in rats is 6 g/kg; the fatal oral dose in humans is estimated to be 450 g. Although some liver tumors were observed in rats fed up to 2000 ppm in the diet, it is not possible to evaluate adequately the carcinogenicity of methoxychlor due to inadequate reporting of these data; three other feeding studies produced no evidence of carcinogenesis. Dogs fed a daily diet containing 4 g/kg body weight developed signs of chlorinated hydrocarbon intoxication, including fasciculations, tremor, hyperesthesia, tonic seizures, and tetanic convulsions after 5 to 8 weeks; most of the dogs died within 3 weeks after onset of effects. Rabbits given 200 mg/kg orally per day died

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after 4 to 5 doses; autopsy findings included mild liver damage and nephrosis. In mice given 5 mg orally over 3 days and in rats given 20 mg, there was a uterotrophic effect manifested as a marked increase in weight of the uterus. There are no reported effects in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 345.7
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.41
4. Vapor density (air = 1 at boiling point of methoxychlor): Not applicable
5. Melting point: 78 or 86 C (172 or 187 F) (dimorphic)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 0.01
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when methoxychlor decomposes.
4. Special precautions: Methoxychlor will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For solids: Dry chemical, water, carbon dioxide, and foam

- **Warning properties**

Since the vapor pressure of this substance is very low, and since methoxychlor decomposes upon heating, warning properties are not considered.
Methoxychlor is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for methoxychlor is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with methoxychlor or liquids containing methoxychlor.
- Non-impervious clothing which becomes contaminated with methoxychlor should be removed promptly and not reworn until the methoxychlor is removed from the clothing.

SANITATION

- Skin that becomes contaminated with methoxychlor should be promptly washed or showered with soap or mild detergent and water to remove any methoxychlor.
- Employees who handle methoxychlor or liquids containing methoxychlor should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methoxychlor may occur and control methods which may be effective in each case:

Operation	Controls
Use as an agricultural insecticide on fruits, vegetables, foliage, crops, and ornamentals; agricultural premises; and animal treatment	Personal protective equipment
Liberation during formulation and manufacture for use as an agricultural insecticide	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Skin Exposure**

If methoxychlor or liquids containing methoxychlor get on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the end of work.

- **Breathing**

If a person breathes in large amounts of methoxychlor, move the exposed person to fresh air at once.

- **Swallowing**

When methoxychlor or liquids containing methoxychlor have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If methoxychlor is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing methoxychlor should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Methoxychlor may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR METHOXYCHLOR

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
150 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, mist, and fume filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust, mist, and fume filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust, mist, and fume filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7500 mg/m³ or less	A powered chemical cartridge respirator with an organic vapor cartridge and a high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3COOCH_3
- Synonyms: Acetic acid methyl ester; methyl acetic ester; methyl ethanoate
- Appearance and odor: Colorless liquid with a fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acetate is 200 parts of methyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 610 milligrams of methyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methyl acetate may cause irritation of the nose, throat, and eyes. Headache, drowsiness, and unconsciousness are also possible. (Several cases of disturbance of vision have been reported from overexposure to this chemical).

2. Long-term Exposure: Prolonged overexposure may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl acetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl acetate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methyl acetate is not known as a kidney toxin in humans, the importance of this organ in the excretion of certain chemicals and their metabolites should be considered before exposing persons with impaired kidney function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapor of methyl acetate is mildly irritating to the upper respiratory tract and, in higher concentrations, to the eyes. Upon absorption, methyl acetate may be hydrolyzed with the liberation of methanol. The systemic effects, especially the chronic effects, may therefore be similar to those of methanol, and could include atrophy of the optic nerve. Animals exposed to concentrations of approximately 10,000 ppm showed narcosis leading to death in some. Chronic poisoning of animals

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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by inhalation resulted in pulmonary edema and changes in liver, kidney, and myocardium. Liquid methyl acetate in the eye causes inflammation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74
2. Boiling point (760 mm Hg): 57 C (135 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of methyl acetate): 2.8
5. Melting point: −98 C (−144 F)
6. Vapor pressure at 20 C (68 F): 173 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 24.5
8. Evaporation rate (butyl acetate = 1): 11.8

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acetate.
4. Special precautions: None

- **Flammability**

1. Flash point: −10 C (14 F) (closed cup)
2. Autoignition temperature: 502 C (935 F)
3. Flammable limits in air, % by volume: Lower: 3.1; Upper: 16
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Summer and May report that the odor threshold of methyl acetate is 200 ppm.
2. Eye Irritation Level: According to Grant, "the vapor at a concentration of 10,000 ppm in air causes irritation of the eyes, nose, and throat in human beings, also in cats." Sax also reports that "the irritant concentration is about 10,000 ppm."
3. Evaluation of Warning Properties: Since the odor threshold of methyl acetate is at the TLV, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl acetate may be used. An analytical method for methyl acetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).
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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl acetate.
- Clothing wet with liquid methyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl acetate, the person performing the operation should be informed of methyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid methyl acetate should be removed immediately and not reworn until the methyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl acetate should be promptly washed or showered to remove any methyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use during preparation of methyl acetone, including methylacetate, methanol, and acetone for use as solvents	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for nitrocellulose and cellulose acetate	General dilution ventilation; personal protective equipment
Liberation during use as a chemical intermediate	General dilution ventilation
Use during spraying of lacquers, paint thinners, and vinyl resin coatings; use of paint removers	Local exhaust ventilation; personal protective equipment
Liberation during preparation of paint removers and lacquer solvents	Local exhaust ventilation; general dilution ventilation
Liberation during preparation of methylacetate or recovery as a by-product from wood carbonization	Local exhaust ventilation
Use during preparation of artificial leather	Local exhaust ventilation; personal protective equipment
Liberation during formulation of lacquers, paints, perfumes, and any vinyl resin coatings	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl acetate gets on the skin, promptly flush the contaminated skin with water. If methyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methyl Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
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RESPIRATORY PROTECTION FOR METHYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. A powered air-purifying chemical cartridge respirator with an organic vapor cartridge. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Acetylene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_3H_4
- Synonyms: Propyne; allylene
- Appearance and odor: Colorless gas with a sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acetylene is 1000 parts of methyl acetylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1650 milligrams of methyl acetylene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acetylene can affect the body if it is inhaled.

- **Effects of overexposure**

Overexposure to methyl acetylene may cause the overexposed person to become drowsy and unconscious.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl acetylene.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to methyl acetylene at potentially hazardous levels.

- **Summary of toxicology**

Methyl acetylene primarily affects the central nervous system. The gas has anesthetic properties at concentrations as high as 42,000 ppm, which is below the LC50 value. At 28,700 ppm for 6 hours daily, 5 days a week for 6 months, most animals survived; there was hyperexcitability, ataxia, tremors, and occasional convulsions, all of which subsided rapidly when the 6-hour exposure period ended. Animals that died or were killed on termination of the study showed pulmonary irritation. Neither acute nor chronic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 40.1
2. Boiling point (760 mm Hg): −23 C (−10 F)
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of methyl acetylene): 1.4
5. Melting point: −103 C (-153 F)
6. Vapor pressure at 20 C (68 F): 3800 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Almost insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable (gas)

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents and chlorine may cause fires and explosions. Methyl acetylene forms compounds with copper and copper alloys that are very sensitive to shock.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acetylene.
4. Special precautions: Copper or copper alloys containing more than 67% copper should not be used in equipment handling methyl acetylene.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 11.7

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4. Extinguishant: Stop flow of gas

- **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: Methyl acetylene is not known to be an eye irritant.

3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for methyl acetylene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid methyl acetylene or from contact with vessels containing methyl acetylene.
- Any clothing which becomes wet with liquid methyl acetylene should be removed immediately and not reworn until the methyl acetylene has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acetylene may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acetylene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during synthesis of pharmaceuticals and aromatics	General dilution ventilation
Liberation during high-temperature, gas-welding operations using MAPP fuel; liberation from decomposition of magnesium carbide by hydrolysis	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of methyl acetylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If methyl acetylene is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak to disperse gas.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, keep people

away, and repair the leak or allow the cylinder to empty.

- Waste disposal methods:

Methyl acetylene may be disposed of

1. If in small quantities, by allowing gas to escape into open air at a place where there are no ignition sources.
2. If in larger quantities, by allowing the gas to burn under the supervision of qualified personnel.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methyl Acetylene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Horn, H. J., Weir, R. J., and Reese, W. H.: "Inhalation Toxicology of Methylacetylene," *A.M.A. Archives of Industrial Health*, 15:20-25, 1957.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR METHYL ACETYLENE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
11,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 11,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Acetylene-Propadiene Mixture

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_3H_4 isomers
- Synonyms: MAPP gas; methyl acetylene-allene mixture; propyne-allene mixture
- Appearance and odor: Colorless gas with a strong, characteristic, foul odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acetylene-propadiene mixture is 1000 parts of methyl acetylene-propadiene mixture per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of methyl acetylene-propadiene mixture per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acetylene-propadiene mixture can affect the body if it is inhaled or if the liquid comes in contact with the skin or eyes

- **Effects of overexposure**

Overexposure to methyl acetylene-propadiene mixture may cause a person to become drowsy or unconscious. Spilled on the skin or in the eyes, it may also cause frostbite.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl acetylene-propadiene mixture.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to methyl acetylene-propadiene mixture at potentially hazardous levels.

- **Summary of toxicology**

Methyl acetylene-propadiene mixture (MAPP) is a gas with anesthetic properties at high concentrations. Animals exposed for 7 hours daily for 16 weeks to 1000 ppm showed no adverse effects; at 5000 ppm there was only slight decline in body and organ weights of some rats, but no pathological changes. In another study of the main component of the mixture, methyl acetylene, rats survived a single 6-hour exposure at 42,000 ppm, which resulted in anesthesia with rapid recovery; autopsy of the rats 9 days after exposure showed bronchiolitis and pneumonitis. Some human subjects indicated that they could detect 25 ppm, and most could detect 100 ppm. The musty odor was considered to be strong at 1000 ppm and quite objectionable at higher concentrations. No adverse effects have been reported from repeated exposures. The liquefied gas may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 40
2. Boiling point (760 mm Hg): −37.8 to −20 C (−36 F to −4 F)
3. Specific gravity (water = 1): 0.576 (liquid)
4. Vapor density (air = 1 at boiling point of methyl acetylene-propadiene mixture): 1.48
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with

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copper alloys containing more than 6% copper may form explosive copper compounds.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acetylene-propadiene mixture.

4. Special precautions: Methyl acetylene-propadiene mixture will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: 454 C (850 F)
3. Flammable limits in air, % by volume: Lower: 3.4; Upper: 10.8
4. Extinguishant: Stop flow of gas

- **Warning properties**

1. Odor Threshold: According to the Biochemical Research Laboratory of the Dow Chemical Company, MAPP has a strong odor which is easily detectable at 100 ppm.
2. Eye Irritation Level: MAPP is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of MAPP is below the permissible exposure limit, MAPP is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- Method

An analytical method for methyl acetylene-propadiene mixture is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid methyl acetylene-propadiene mixture or from contact with vessels containing liquid methyl acetylene-propadiene mixture.
- Any clothing which becomes wet with liquid methyl acetylene-propadiene mixture should be removed immediately and not reworn until the methyl acetylene-propadiene mixture has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acetylene-propadiene mixture may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acetylene-propadiene mixture may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from flame hardening, metallizing, brazing, welding and cutting	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid methyl acetylene-propadiene mixture gets into the eyes, flush eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Do not use hot water for eye flushing. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid methyl acetylene-propadiene mixture gets on the skin, immediately flush the contaminated skin with water. If liquid methyl acetylene-propadiene mixture soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl acetylene-propadiene mixture, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If methyl acetylene-propadiene mixture is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

- Waste disposal method:

Methyl acetylene-propadiene mixture may be disposed of by burning at a safe location or in a suitable combustion chamber.

- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methylene Acetylene-Propadiene Mixture," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Dow Chemical Company, Biochemical Research Laboratory: *Material Safety Data Sheet – Methyl Acetylene-Propadiene Mixture*, Midland, Michigan, 1964.
- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.
- Torkelson, T. R., and Rowe, V. K.: "Results of Repeated Inhalation by Laboratory Animals and a Limited Human Sensory Study of a Mixture of Saturated and Unsaturated C_3 and C_4 Hydrocarbons (MAPP Industrial Gas)," *American Industrial Hygiene Association Journal*, 25:554-559, 1964.
- Underwriters' Laboratories: *Methyl Acetylene-Propadiene Mixture.*

RESPIRATORY PROTECTION FOR METHYL ACETYLENE-PROPADIENE MIXTURE

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Vapor Concentration	
5000 ppm or less	A gas mask with a chin-style canister providing protection against methyl acetylene-propadiene mixture.
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
20,000 ppm or less	A gas mask with a front- or back-mounted canister providing protection against methyl acetylene-propadiene mixture. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against methyl acetylene-propadiene mixture. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Acrylate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_2=CHCOOCH_3$
- Synonyms: Methyl propenoate
- Appearance and odor: Clear, colorless liquid with a sharp, sweet, and fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acrylate is 10 parts of methyl acrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of methyl acrylate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acrylate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methyl acrylate may cause irritation of the eyes, nose, throat, and lungs. Death may be caused by lung damage from breathing high air levels or from swallowing it.

2. Long-term Exposure: Prolonged contact with the skin or eyes may result in severe damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl acrylate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl acrylate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl acrylate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl acrylate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl acrylate is absorbed through the skin. It also is a defatting agent and can cause drying and cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methyl acrylate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methyl acrylate is not known as a kidney toxin in humans, the importance of this organ in the excretion of certain chemicals and their metabolites should be considered before exposing persons with impaired kidney function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapor of methyl acrylate is irritating to the conjunctiva and upper respiratory tract. In moderate concentrations there are characteristic lacrimatory effects in man. Animals exposed to high concentrations show marked irritation of the eyes and of the respiratory tract, leading to pulmonary edema. The lowest concentration of vapor producing no significant effect in rodents is 30 ppm. Prolonged contact with the eye or the skin in animals causes severe damage. Skin sensitiza-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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tion probably occurs, and fatal doses of the liquid are absorbed through the skin of animals exposed for 24 hours. There are no reports of injury to man from long-term exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 86
2. Boiling point (760 mm Hg): 80 C (176 F)
3. Specific gravity (water = 1): 0.96
4. Vapor density (air = 1 at boiling point of methyl acrylate): 2.95
5. Melting point: −75 C (−103 F)
6. Vapor pressure at 20 C (68 F): 68.2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 5.5
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat and/or lack of appropriate inhibitor concentration can cause methyl acrylate to polymerize violently and burst container.
2. Incompatibilities: Contact with nitrates and other oxidizing materials, including peroxides and other initiators of polymerization, strong alkalies, and atmospheric moisture may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acrylate.
4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.

- **Flammability**

1. Flash point: −7.8 C (18 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 25
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The Manufacturing Chemists Association states that most persons can detect the odor of methyl acrylate at 20 ppm. "Odor detection has little practical value in chronic repeated exposures, since most workers become less sensitive to the odor and will tolerate atmospheric concentrations greater than the threshold limits."
2. Eye Irritation Level: The MCA states that "irritation of the eyes and mucous membranes is experienced beginning at about 75 ppm."
3. Evaluation of Warning Properties: Methyl acrylate has poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl acrylate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl acrylate may be used. An analytical method for methyl acrylate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid methyl acrylate.
- Clothing wet with liquid methyl acrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl acrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl acrylate, the person performing the operation should be informed of methyl acrylate's hazardous properties.

- Where there is any possibility of exposure of an employee's body to liquid methyl acrylate, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with liquid methyl acrylate should be removed immediately and not reworn until the methyl acrylate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acrylate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl acrylate should be immediately washed or showered to remove any methyl acrylate.
- Employees who handle liquid methyl acrylate should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acrylate may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of thermoplastic coatings; use in manufacture of acrylic fibers; use in synthesis of higher acrylates; during preparation of adhesives and sealants based on methyl acrylate	Local exhaust ventilation; personal protective equipment
Use during polymerization in aqueous emulsions to produce resins for surface coatings and adhesives; use during polymerization in solutions to produce resins for surface coatings and adhesives	Local exhaust ventilation; personal protective equipment
Use during preparation of amphoteric surfactants for use in hair shampoos	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl acrylate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl acrylate gets on the skin, immediately flush the contaminated skin with water. If methyl acrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl acrylate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible. Properly trained individuals may assist the affected person by administering 100% oxygen.

- **Swallowing**

When methyl acrylate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl acrylate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl acrylate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl acrylate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methyl Acrylate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYL ACRYLATE

Condition	**Minimum Respiratory Protection* Required Above 10 ppm**
Vapor Concentration	
75 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Methylal

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3OCH_2OCH_3$
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetal formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylal can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to methylal may cause irritation of the eyes, nose, and throat, lightheadedness, incoordination, and unconsciousness.

2. *Long-term Exposure:* Prolonged overexposure to methylal may cause irritation of the skin.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylal.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylal at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylal exposure.

—Skin disease: Methylal is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylal might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

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Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76
2. Boiling point (760 mm Hg): 44 C (111 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of methylal): 2.6
5. Melting point: −105 C (−157 F)
6. Vapor pressure at 20 C (68 F): 330 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): 23.1

- **Reactivity**

1. Conditions contributing to instability: Heat, presence of acids
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18 C (−4 F) (closed cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylal.
- Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or

otherwise cleaned to remove the methylal, the person performing the operation should be informed of methylal's hazardous properties.

- Any clothing which becomes wet with liquid methylal should be removed immediately and not reworn until the methylal is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylal may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxy-acids	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines	General dilution ventilation; process enclosure; personal protective equipment
Use as a reaction solvent with acetylene or in Grignard and Reppe reaction; use as a source of formaldehyde and methanol	General dilution ventilation; process enclosure; personal protective equipment
Use as a methylating agent or chemical intermediate	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of perfume	General dilution ventilation; process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methylal gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylal, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methylal has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylal is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Methylal may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYLAL

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3OH
- Synonyms: Methanol; wood alcohol; Columbian spirits; carbinol
- Appearance and odor: Colorless liquid with a characteristic, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl alcohol is 200 parts of methyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 260 milligrams of methyl alcohol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 200 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 800 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Methyl Alcohol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Swallowing methyl alcohol or breathing very high concentrations of methyl alcohol may produce headache, weakness, drowsiness, lightheadedness, nausea, vomiting, drunkenness, and irritation of the eyes, blurred vision, blindness, and death. A person may get better and then worse again up to 30 hours later.

2. Long-term Exposure: Prolonged exposure to higher concentrations of methyl alcohol may result in headaches, burning of the eyes, dizziness, sleep problems, digestive disturbances, and failure of vision. Repeated or prolonged skin exposure may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl alcohol at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, and eyes should be stressed.

—Skin disease: Methyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be susceptible to the effects of this agent.

—Liver function tests: Methyl alcohol may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Although methyl alcohol has not been proven to be kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Eye disease: Because methyl alcohol may cause optic atrophy and blindness, those with pre-existing eye diseases may be at increased risk from exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. In addition, anyone developing the above-listed conditions or who has been splashed in the eyes with,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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has ingested, or otherwise has been exposed to methyl alcohol should be placed under medical surveillance.

- **Summary of toxicology**

Ingestion of methyl alcohol is a well-known cause of optic neuropathy and may be lethal. Severe acidosis may result from ingestion or high exposures. Animals exposed to vapor concentrations above 8000 to 10,000 ppm show narcotic effects progressing from lethargy, to ataxia, to prostration and death in a state of profound acidosis due in part to the metabolic formation of formaldehyde and formic acid. Occupational exposure to high concentrations of methyl alcohol vapor has been reported to cause death or blindness, usually from working in a confined space. A woman died after exposure for 12 hours to vapor concentrations calculated at 4000 to 13,000 ppm. Chronic poisoning manifested by marked diminution of vision and enlargement of the liver has been reported in a workman exposed at levels of 1200 to 8000 ppm for a period of 4 years. Direct skin contact with methy alcohol may cause dermatitis, erythema, and scaling.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 32
2. Boiling point (760 mm Hg): 64.5 C (148 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of methyl alcohol): 1.1
5. Melting point: −98 C (-144 F)
6. Vapor pressure at 20 C (68 F): 97 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 5.9

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and formaldehyde) may be released in a fire involving methyl alcohol.
4. Special precautions: Methyl alcohol will attack some forms of plastics, rubber, and coatings. It may also react with metallic aluminum at high temperatures.

- **Flammability**

1. Flash point: 11 C (52 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 36
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May and Summer report that the odor threshold of methyl alcohol (methanol) is 5900 ppm. The AIHA *Hygienic Guide* states that the odor is faint at 2000 ppm.
2. Eye Irritation Level: The *Hygienic Guide* states that irritation occurs only at high concentrations. Grant states that "external contact of methanol with the eye has been alleged to have caused corneal opacities, but this must be far from the rule . . . . By exposure of cats to methanol vapors an attempt has been made to induce vacuoles in the corneal epithelium similar to those produced by other solvents, but this has been unsuccessful."

Browning reports that concentrations ranging from 7500 ppm to 69,000 ppm irritate mucous membranes.

3. Evaluation of Warning Properties: Methyl alcohol (methanol) has poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methyl alcohol. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of methyl alcohol in an adsorption tube containing silica gel, followed by desorption with water, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl alcohol may be used. An analytical method for methyl alcohol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl alcohol.
- Clothing wet with liquid methyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl alcohol, the person performing the operation should be informed of methyl alcohol's hazardous properties.
- Any clothing which becomes wet with liquid methyl alcohol should be removed immediately and not reworn until the methyl alcohol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl alcohol should be promptly washed or showered to remove any methyl alcohol.
- Eating and smoking should not be permitted in areas where liquid methyl alcohol is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during application of surface coatings such as shellac, wood dyes, nitrocellulose lacquers, water-proofing formulations, and phenolic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for rotogravure inks, aniline dyes, and duplicator fluids	General dilution ventilation
Liberation during manual application of methanol as a cleaner for coated surfaces, leather, gloves, and metal and resins surfaces prior to further treatment	General dilution ventilation; personal protective equipment
Liberation during manufacture of formaldehyde by oxidation or dehydrogenation	Local exhaust ventilation; general dilution ventilation
Use in plastics industry to produce plasticizers, softening agents, and acrylic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use as an intermediate in the preparation of methacrylates, methyl chlorides, methyl ethers, dimethyl sulfate, methyl formate, and methyl bromide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during application as an extractant in industrial chemical processes such as refinery gasoline and oils and purifying pharmaceuticals such as steroids and hormones	Local exhaust ventilation; general dilution ventilation
Use as a solvent in rubber industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl alcohol gets on the skin, promptly flush the contaminated skin with water. If methyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
10,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 25,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3NH_2
- Synonyms: Monomethylamine; anhydrous methylamine
- Appearance and odor: Colorless gas with an odor like ammonia, but more fishy, particularly at lower concentrations. It can be stored under pressure as a liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylamine is 10 parts of methylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of methylamine per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylamine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Methylamine may cause irritation of the eyes, nose, throat, and lungs. It may also cause coughing and sneezing. Both the liquid and vapor of methylamine are highly irritating to the eyes. Eye injury may occur if proper care is not given immediately. Methylamine solutions may burn the skin.

2. Long-term Exposure: Repeated or prolonged exposure to methylamine may cause irritation of the skin or eyes.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylamine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Methylamine causes eye damage in animals and eye irritation in humans. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Methylamine in solution is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylamine gas is a severe eye and respiratory irritant. The LD50 was 0.1 to 0.2 g/kg in rats exposed orally to a 40% aqueous solution of methylamine. One case of bronchitis in a chemical worker has been reported; concentrations measured in the workroom ranged from 2 to 60 ppm; the duration of the exposure was not given. Brief exposures to 20 to 100 ppm are said to produce transient irritation of the eyes, nose, and throat. No symptoms of irritation are produced from longer exposures at less than 10 ppm. One drop of 5% aqueous solution caused conjunctival hemorrhage, superficial corneal opacities, and edema in experimental animals; a

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40% solution caused corneal damage in rabbits. A 40% solution caused necrosis when applied to the skin of a rabbit. Dermatitis and conjunctivitis are occasionally observed in workers after prolonged exposure to the vapor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 31.1
2. Boiling point (760 mm Hg): −6.32 C (20.6 F)
3. Specific gravity (water = 1): 0.656
4. Vapor density (air = 1 at boiling point of methylamine): 1.1
5. Melting point: −93.5 C (-136.3 F)
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 25 C (77 F): 959 cc/100 ml
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of gas or liquid methylamine with mercury or with strong oxidizers will cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving methylamine.
4. Special precautions: Liquid methylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: 430 C (806 F)
3. Flammable limits in air, % by volume: Lower: 5; Upper: 21
4. Extinguishant: Stop flow of gas; use carbon dioxide, alcohol foam, or dry chemical for water solutions

- **Warning properties**

1. Odor Threshold: May reports an odor threshold of 3.3 ppm. Patty reports that "olfactory fatigue occurs readily" upon exposure to methylamine.
2. Eye Irritation Level: Grant reports that methylamine is an eye irritant, but the concentrations producing irritation are not given. Patty, however, reports that "brief exposures to 20 to 100 ppm produce transient eye . . . irritation."
3. Other Information: Patty reports that transitory nose and throat irritation is caused by short exposures to 20 to 100 ppm.
4. Evaluation of Warning Properties: Although the odor threshold of methylamine (3.3 ppm) is well below the permissible exposure limit, methylamine is treated as a material with poor warning properties, since "olfactory fatigue occurs readily." In addition, the irritant effects produced by brief exposures to methylamine are not considered to give adequate warning, since these effects are only transient.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for methylamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming contaminated with liquid methylamine or solutions containing methylamine or from becoming frozen from contact with vessels containing methylamine.
- Clothing wet with liquid methylamine or solutions containing methylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylamine, the person performing the operation should be informed of methylamine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid methylamine or solutions

containing methylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Any clothing which becomes wet with methylamine or non-impervious clothing which becomes contaminated with methylamine should be removed immediately and not reworn until the methylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid methylamine or solutions containing methylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid methylamine or solutions containing methylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with methylamine should be immediately washed or showered to remove any methylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical intermediate in production of insecticides, herbicides, and fungicides; use as a chemical intermediate in production of surfactants	Local exhaust ventilation; general dilution ventilation
Use in production of rocket fuels and explosives	Local exhaust ventilation; general dilution ventilation
Use in production of pharmaceuticals and photographic chemicals; intermediate for dyes, textiles, dye assists, rubber, and anti-corrosive chemicals	Local exhaust ventilation; general dilution ventilation
Use as a polymerization inhibitor of hydrocarbons during distillization; use to prevent coagulation and webbing in natural and synthetic latex; use to prevent polymerization in paint removers	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid methylamine or solutions containing methylamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid methylamine or solutions containing methylamine get on the skin, immediately flush the contaminated skin with water. If liquid methylamine or solutions containing methylamine soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When a solution of methylamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

- If methylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak to disperse gas.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

- Waste disposal method:

Methylamine may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR METHYLAMINE

Condition	**Minimum Respiratory Protection* Required Above 10 ppm**
Gas Concentration	
100 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against methylamine. Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

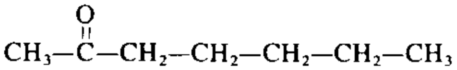
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR METHYL (n-AMYL) KETONE

INTRODUCTION

This guideline summarizes pertinent information about methyl (n-amyl) ketone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_7H_{14}O$
- **Structure:**



$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

- **Synonyms:** n-Amyl methyl ketone, 2-heptanone
- **Identifiers:** CAS 110-43-0; RTECS MJ5075000; DOT 1110
- **Appearance and odor:** Clear, colorless liquid with a penetrating, fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.21
2. Boiling point (at 760 mmHg): 151°C (304°F)
3. Specific gravity (water = 1): 0.82
4. Vapor density [air = 1 at boiling point of methyl (n-amyl) ketone]: 3.93
5. Melting point: -35°C (-31°F)
6. Vapor pressure at 20°C (68°F): 2 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.43
8. Evaporation rate (butyl acetate = 1): 0.4
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.27% (2,700 ppm)
10. Ionization potential: 9.33 eV

- **Reactivity**

1. Incompatibilities: Contact with strong acids, alkalies, and oxidizing agents may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving methyl (n-amyl) ketone.
3. Caution: Methyl (n-amyl) ketone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 39°C (102°F) (closed cup)
2. Autoignition temperature: 393°C (740°F)
3. Flammable limits in air, % by volume: Lower, 1.1; upper, 7.9
4. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.35 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, methyl (n-amyl) ketone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for methyl (n-amyl) ketone is 100 parts of methyl (n-amyl) ketone per million parts of air (ppm) [465 milligrams of methyl (n-amyl) ketone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 100 ppm (465 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (235 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for methyl (n-amyl) ketone

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	100	465
NIOSH REL TWA	100	465
ACGIH TLV® TWA	50	235

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HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl (n-amyl) ketone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute inhalation of methyl (n-amyl) ketone by guinea pigs caused irritation of the mucous membranes, narcosis, and death.

- **Signs and symptoms of exposure**

1. *Short-term exposure (acute):* Exposure to methyl (n-amyl) ketone can cause headaches, dizziness, and irritation of the eyes, nose, and throat.
2. *Long-term exposure (chronic):* Exposure to methyl (n-amyl) ketone can cause dryness and irritation of the skin.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to methyl (n-amyl) ketone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to methyl (n-amyl) ketone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to methyl (n-amyl) ketone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to methyl (n-amyl) ketone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting methyl (n-amyl) ketone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure methyl (n-amyl) ketone may also be used if available. A detailed sampling and analytical method for methyl (n-amyl) ketone may be found in the *NIOSH Manual of Analytical Methods* (method number 1301).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with methyl (n-amyl) ketone.

Workers should be provided with and required to use splash-proof safety goggles where methyl (n-amyl) ketone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with methyl (n-amyl) ketone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl (n-amyl) ketone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of methyl (n-amyl) ketone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with methyl (n-amyl) ketone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle methyl (n-amyl) ketone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to methyl (n-amyl) ketone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for methyl (n-amyl) ketone

Operations	Controls
During use in the spray application of lacquers	Local exhaust ventilation, personal protective equipment
During use in the preparation of synthetic resins, especially for metal roll-coating	Process enclosure, local exhaust ventilation
During use as a solvent for rubber and nitrocellulose	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to methyl (n-amyl) ketone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If methyl (n-amyl) ketone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to methyl (n-amyl) ketone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If methyl (n-amyl) ketone gets on the skin, wash it immediately with soap and water. If methyl (n-amyl) ketone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If methyl (n-amyl) ketone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing methyl (n-amyl) ketone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from methyl (n-amyl) ketone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing methyl (n-amyl) ketone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Methyl (n-amyl) ketone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

5. Liquids containing methyl (n-amyl) ketone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for methyl (n-amyl) ketone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 2,500 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 4,000 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 4,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 100 ppm (465 mg/m^3) (TWA).

Occupational Health Guideline for Methyl Bromide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3Br
- Synonyms: Bromomethane
- Appearance and odor: Colorless liquid or or gas with a chloroform-like odor at high concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl bromide is a ceiling of 20 parts of methyl bromide per million parts of air (ppm). This may also be expressed as 80 milligrams of methyl bromide per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl bromide from 15 ppm to 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl bromide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Methyl bromide may cause headache, dizziness, nausea, vomiting, blurred vision, slurred speech, and convulsions. High concentrations may cause unconsciousness and death. High concentrations may also cause lung irritation resulting in congestion with coughing, chest pain, and shortness of breath. Lung effects may be delayed in onset. Exposure may also result in kidney damage. The liquid splashed on clothing, gloves, or shoes may be held in close contact with the skin and result in skin burns. Blisters commonly appear after several hours. If the exposure is less severe, an itching skin rash may appear after several days. Contact of liquid methyl bromide with the eyes may cause serious injury.

2. Long-term Exposure: Prolonged or repeated exposure to methyl bromide may cause a variety of symptoms and signs mostly due to injury of the central nervous system. These include visual disturbances, slurred speech, numbness of the arms and legs, confusion, shaking, and unconsciousness. The symptoms may stop within a few days after the termination of exposure or may last for several months. Usually recovery is complete.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl bromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl bromide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. A careful history and examination of the nervous and respiratory systems should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Methyl bromide may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methyl bromide is reported to cause pulmonary impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Methyl bromide gas is a severe pulmonary irritant and neurotoxin. It is also a narcotic at high concentrations. Rats did not survive when exposed to 12,850 ppm for 6 minutes, but did survive following exposure to 260 ppm for 8 hours; the no-effect level on repeated exposure was 16 ppm for all species. There are numerous reports of human intoxication from accidental exposure associated with its use in fire extinguishers and as a fumigant. Estimates of concentrations which have caused human fatalities range from 8000 ppm for a few hours to 60,000 ppm for a brief exposure. The onset of toxic symptoms is usually delayed, and the latent period may be from 30 minutes to several days. Early symptoms include headache, visual disturbances, nausea, vomiting, and malaise. In some cases eye irritation, vertigo, and tremors of the hands have occurred; the tremors may progress to twitchings and finally to convulsions. The onset of dyspnea may herald the development of pulmonary edema. Tubular damage in the kidneys has been observed in fatal cases. Some who recovered from severe intoxication have had persistent central nervous system effects including vertigo, depression, hallucinations, anxiety, and inability to concentrate. The determination of bromide in human blood has been proposed for the purpose of estimating the severity of exposure; in a few cases, levels of 40 mg/100 ml of blood have been associated with gross disability, while levels of 10 mg/100 ml and less have been followed by complete recovery. The procedure has not been sufficiently verified to recommend it for routine monitoring of occupational exposure. Local contact with the eye by the gas or liquid results in transient irritation and conjunctivitis. Repeated splashes of the liquid on the skin cause marked irritation with vesiculation; less severe exposures result in a dry, scaling, itching dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 94.9
2. Boiling point (760 mm Hg): 3.6 C (38.4 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of methyl bromide): 3.3
5. Melting point: −94 C (−137 F)
6. Vapor pressure at 20 C (68 F): 1.83 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with aluminum or strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide and carbon monoxide) may be released in a fire involving methyl bromide.
4. Special precautions: Liquid methyl bromide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: None in standard test method
2. Autoignition temperature: 537 C (999 F)
3. Flammable limits in air, % by volume: (Only in presence of high energy ignition source) Lower: 13.5; Upper: 14.5
4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: Both Patty and the AIHA *Hygienic Guide* report that methyl bromide has practically no odor. Grant notes, however, that at extremely high concentrations, methyl bromide has a "sweetish, not unpleasant odor."
2. Eye Irritation Level: Grant reports that methyl bromide "causes no immediate irritation of the eyes, . . . even at severely poisonous concentrations." Following a period of several hours after exposure to the gas, however, the victim may "have lacrimation from irritation of the eyes." Grant states that "local contact of methyl bromide with the eye, either as concentrated vapor or as a splash of liquid, has resulted in no more than transient irritation and conjunctivitis in the few cases in which this accident has been observed." He also reports that exposing a rabbit's eye to pure methyl bromide gas for 1-1/2 minutes resulted in an "immediate loss of surface luster, followed in several hours by a loss of corneal epithelium and much edema of the conjunctivae and lids." The cornea became opaque but began clearing within 5 days. Grant notes that this exposure was far more severe than that which would happen by accident.
3. Other Information: Grant reports that methyl bromide causes no immediate irritation of the "nose or respiratory tract, even at severely poisonous concentrations."
4. Evaluation of Warning Properties: Since methyl bromide has virtually no odor and no immediately irritating effects, it has poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methyl bromide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl bromide may be used. An analytical method for methyl bromide is in the *NIOSH* obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set J" (order number PB 263 959).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid methyl bromide.
- Clothing contaminated with liquid methyl bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl bromide, the person performing the operation should be informed of methyl bromide's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid methyl bromide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid methyl bromide should be removed immediately and not reworn until the methyl bromide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl bromide may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl bromide should be immediately washed or showered with soap or mild detergent and water to remove any methyl bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a space and soil fumigant in agriculture and industry	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in food sterilization for pest control in fruits, vegetables, dairy products, nuts, and grains	General dilution ventilation; local exhaust ventilation
Use in organic synthesis as methylating agent, for preparation of quarternary ammonium compounds and organo-tin derivatives; use as selective solvent in aniline dyes; laboratory procedures	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl bromide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl bromide gets on the skin, immediately flush the contaminated skin with water. If methyl bromide soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl bromide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl bromide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl bromide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

- Waste disposal method:

Methyl bromide may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR METHYL BROMIDE

Condition	**Minimum Respiratory Protection*** **Required Above 20 ppm**
Gas Concentration	
200 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Cellosolve

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3OCH_2CH_2OH$
- Synonyms: 2-Methoxyethanol; glycol monomethyl ether; ethylene glycol monomethyl ether; methyl oxitol; Ektasolve; Jeffersol EM
- Appearance and odor: Colorless liquid with a mild, non-residual odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl cellosolve is 25 parts of methyl cellosolve per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 80 milligrams of methyl cellosolve per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl cellosolve can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin. It may enter the body through the skin.

- **Effects of overexposure**

1\. *Short-term Exposure:* Overexposure to methyl cellosolve may cause irritation of the eyes, nose, and throat, drowsiness, weakness, and shaking. Swallowing methyl cellosolve may be fatal.

2\. *Long-term Exposure:* Prolonged or repeated exposure may cause headache, drowsiness, weakness, fatigue, staggering, personality change, and decreased mental ability. Anemia and other blood changes may result.

3\. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl cellosolve.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl cellosolve at potentially hazardous levels:

1\. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system should be stressed.

—A complete blood count: This compound has been shown to affect the hematopoietic system. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: This compound has caused acute kidney damage in animals and in humans after oral ingestion.

2\. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methyl cellosolve exerts its effects primarily on the hematopoietic and central nervous systems, although the vapor is also a mild irritant. Cases of toxic encephalopathy and macrocytic anemia have been reported from industrial exposures that may have been as low as 25 to 75 ppm. Symptoms were headache, drowsiness, lethargy, and weakness. Manifestations of central nervous system instability included ataxia, dysarthria, tremor, and somnolence. These effects are usually reversible. In acute exposures the central nervous system effects were the more pronounced, while prolonged exposure to lower concentrations produced primarily evidence of depression of erythrocyte formation. Anemia may be pronounced. When exposure was re-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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duced to 20 ppm, no further cases occurred. The LC50 for 7-hour exposures of rats was 1480 ppm; death was due to lung and kidney injury. Rabbits exposed to 800 ppm and 1600 ppm for 4 to 10 days showed irritation of the upper respiratory tract and lungs, severe glomerulonephritis, hematuria, and albuminuria. Instilled in rabbit eyes, it caused immediate pain, conjunctival irritation, and slight corneal cloudiness which cleared in 24 hours.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76.1
2. Boiling point (760 mm Hg): 124 C (256 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of methyl cellosolve): 2.6
5. Melting point: −85 C (−121 F)
6. Vapor pressure at 20 C (68 F): 6 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Approximately 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with strong caustics may cause decomposition.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl cellosolve.
4. Special precautions: Methyl cellosolve will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 42 C (107 F) (closed cup)
2. Autoignition temperature: 285 C (545 F)
3. Flammable limits in air, % by volume: Lower: 2.5; Upper: 19.8
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for methyl cellosolve of 60 ppm.
2. Eye Irritation Level: Grant states that methyl cellosolve, "tested by applying three drops to rabbit eyes, . . . was found to be only slightly irritating, causing only temporary, slight reddening of the conjunctiva." Browning states that the "vapor of methyl cellosolve is irritant to mucous membranes," but does not give concentrations producing this irritation.
3. Evaluation of Warning Properties: Although the odor threshold of methyl cellosolve is within three times the permissible exposure limit, odor is not considered an adequate warning property. Browning reports that cases of toxic encephalopathy and macrocytic anemia have been reported among workers exposed to concentrations as low as 25 to 75 ppm methyl cellosolve. The latter was present in a solvent mixture including ethanol and cellulose acetate, however.

The AIHA *Hygienic Guide* states that "warning properties, both odor and irritation, are not sufficient to prevent exposure to concentrations which are physiologically significant."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl cellosolve vapors using an adsorption tube with subsequent desorption with methanol in methylene chloride and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl cellosolve may be used. An analytical method for methyl cellosolve is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent repeated or prolonged skin contact with liquid methyl cellosolve.

- Clothing contaminated with liquid methyl cellosolve should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl cellosolve from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl cellosolve, the person performing the operation should be informed of methyl cellosolve's hazardous properties.
- Where exposure of an employee's body to liquid methyl cellosolve may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid methyl cellosolve and any clothing which becomes wet with liquid methyl cellosolve should be removed immediately and such clothing should not be reworn until the methyl cellosolve is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl cellosolve may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid methyl cellosolve should be immediately washed or showered to remove any methyl cellosolve.
- Employees who handle liquid methyl cellosolve should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl cellosolve may occur and control methods which may be effective in each case:

Operation	Controls
Use during spray application or other method involving heat of surface coatings containing solvent, including wood- and wire-coating lacquers, metal coatings, alkyd baking enamels, phenolic varnishes, and epoxy resin coatings	Local exhaust ventilation; personal protective equipment
Use in printing on plastic materials, rotogravure printing, and cellulose acetate pigment printing on textiles	General dilution ventilation; personal protective equipment
Use during non-heat related application of surface coatings containing solvent, including varnishes and lacquers	Local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings and dyeing agents for stains, lacquers, dyes, and inks	Process enclosure; local exhaust ventilation
Liberation during sealing of moisture-proof cellophane wrappers and packaging	Process enclosure
Liberation during dyeing operations, including cellulose acetate fibers and fabric, rayon, leather dyeing, and wood staining	Process enclosure; general dilution ventilation
Use as an anti-icing agent in JP-4 military jet fuel and as an anti-stall additive in gasoline	General dilution ventilation
Liberation during synthesis of plasticizer and other compounds	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl cellosolve gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl cellosolve gets on the skin, promptly wash the contaminated skin with water. If methyl cellosolve soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl cellosolve, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl cellosolve has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl cellosolve is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl cellosolve should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Methyl cellosolve may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methyl Cellosolve," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYL CELLOSOLVE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
250 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
1250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Methyl Cellosolve Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOCH_2CH_2OCH_3$
- Synonyms: 2-Methoxyethyl acetate; glycol monomethyl ether acetate; ethylene glycol monomethyl ether acetate
- Appearance and odor: Colorless liquid with a mild, ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl cellosolve acetate is 25 parts of methyl cellosolve acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 120 milligrams of methyl cellosolve acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl cellosolve acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

Swallowing a large single dose of methyl cellosolve acetate might be fatal. Swallowing repeated smaller doses of methyl cellosolve acetate or repeated breathing of high air levels of methyl cellosolve acetate might cause lung or kidney damage, brain damage, and death. It is unlikely that air levels of methyl cellosolve acetate will be dangerous unless the liquid is heated. Methyl cellosolve acetate might cause eye irritation if splashed in the eyes. Methyl cellosolve acetate can be absorbed through intact skin. If a large amount is absorbed, death may result.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl cellosolve acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl cellosolve acetate at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl cellosolve acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl cellosolve acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl cellosolve acetate is absorbed through the skin. It also is a defatting agent and may cause dryness and cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Since methyl cellosolve acetate may cause kidney damage in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although methyl cellosolve acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methyl cellosolve acetate is irritating to the upper respiratory tract and is only slightly narcotic. Guinea

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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pigs and cats exposed to nearly saturated vapor died after some delay; concentrations of 1500 ppm for 7 hours killed cats, while 7000 ppm for 4 hours was lethal to some rats. On repeated exposures, 500 ppm for 8 hours killed some cats. There was irritation of upper respiratory tract, disturbance of equilibrium, drowsiness, and apathy followed by death. These animals had damage to the lung and kidney. There was only slight irritation of the eyes. There was no irritation upon skin contact, but absorption did occur. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 118
2. Boiling point (760 mm Hg): 145 C (293 F)
3. Specific gravity (water = 1): 1.01
4. Vapor density (air = 1 at boiling point of methyl cellosolve acetate): 4.1
5. Melting point: −65 C (−85 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Completely miscible
8. Evaporation rate (butyl acetate = 1): 0.3

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl cellosolve acetate.
4. Special precautions: None

- **Flammability**

1. Flash point: 44 C (111 F) (closed cup)
2. Autoignition temperature: 393 C (740 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.2
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: According to the *Handbook of Organic Industrial Solvents*, the odor threshold of methyl cellosolve acetate is twice the permissible exposure level.
2. Eye Irritation Level: According to Browning, methyl cellosolve acetate is only slightly irritating to the eyes and mucous membranes. No quantitative information is available concerning what concentrations produce the irritation, however. Union Carbide reports that "five drops of undiluted chemical produced minor injury in rabbit eyes."
3. Evaluation of Warning Propertes: Since the odor threshold of methyl cellosolve acetate is only twice the permissible exposure level, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl cellosolve acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl cellosolve acetate may be used. An analytical method for methyl cellosolve acetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl cellosolve acetate.
- Clothing wet with liquid methyl cellosolve acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the

removal of methyl cellosolve acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl cellosolve acetate, the person performing the operation should be informed of methyl cellosolve acetate's hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid methyl cellosolve acetate should be removed promptly and not reworn until the methyl cellosolve acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl cellosolve acetate may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid methyl cellosolve acetate should be promptly washed or showered to remove any methyl cellosolve acetate.
- Employees who handle liquid methyl cellosolve acetate should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl cellosolve acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent during spray or heat applications of surface coatings, including varnishes, dopes, lacquers, metal lacquers, cellulose lacquers for paper coatings, textile printing, and leather finishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent during spray or heat applications of adhesives, including polyvinyl formal, polyvinyl butyral, and polyvinyl acetate adhesives	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photographic film	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during dry cleaning operations	Local exhaust ventilation; personal protective equipment
Use as a solvent during manufacture of surface coatings, including lacquers, dopes, varnishes, nail polishes; use during manufacture of adhesives	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl cellosolve acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl cellosolve acetate gets on the skin, promptly flush the contaminated skin with water. If methyl cellosolve acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl cellosolve acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl cellosolve acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl cellosolve acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.

2. Ventilate area of spill or leak.

3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Liquid methyl cellosolve acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl cellosolve acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methyl Cellosolve Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYL CELLOSOLVE ACETATE

Condition	**Minimum Respiratory Protection* Required Above 25 ppm**
Vapor Concentration	
250 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
4500 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 4500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Chloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3Cl
- Synonyms: Chloromethane
- Appearance and odor: Colorless gas with a faint, sweet odor that is not noticeable at dangerous concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl chloride is 100 parts of methyl chloride per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and a maximum acceptable peak of 300 ppm for 5 minutes in any three-hour period. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl chloride from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl chloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Deaths have occurred following single severe or repeated prolonged moderate overexposure. Overexposure may cause dizziness, vomiting, abdominal pain, diarrhea, breathing difficulties, and unconsciousness. Convulsions and disturbances of vision may occur. It may also damage the kidneys, liver, or blood. The symptoms of methyl chloride overexposure are usually delayed in onset. Frostbite may occur from contact with liquefied methyl chloride.

2. Long-term Exposure: Repeated moderate or mild overexposure may cause delayed (24 to 48 hours) onset of dizziness, headache, mental confusion, slurred speech, double vision, and sleepiness. Recovery from the effects of exposure to this chemical may be slow.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl chloride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver, and kidneys should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methyl chloride vapor is a narcotic and may cause a toxic encephalopathy. The LC50 for mice for 7-hour exposure was approximately 3000 ppm. At this concentration some species showed pulmonary edema with hemorrhage, moderate centrolobular necrosis of the liver, and tubular damage in the kidney. At 500 ppm repeated daily for 6 hours, there was response in some species, while 300 ppm daily for 64 weeks produced no detectable effects. Human fatalities have occurred from a single severe exposure or less severe prolonged exposures. Severe but nonfatal poisoning in man is characterized by a latent period of several hours, followed by dizziness, nausea, vomiting, double vision, weakness, paralysis, convulsions, and coma; renal or hepatic

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damage and anemia also occur. Some workers exposed daily to concentrations averaging 195 to 475 ppm showed delayed signs, including weakness, drowsiness, staggering gait, slurred speech, lapses of memory, and cyanosis. The onset is often insidious and may be confused with mild viral illness; more severe intoxication has been mistaken for viral encephalitis or heavy-metal poisoning. Effects may last for a long period following exposure. No effects were seen in other workers exposed to 15 to 195 ppm. Frostbite may result from contact with the liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 50.5
2. Boiling point (760 mm Hg): −24.2 C (−11.6 F)
3. Specific gravity (water = 1): 0.92 (liquid)
4. Vapor density (air = 1 at boiling point of methyl chloride): 1.8
5. Melting point: −97.6 C (−144 F)
6. Vapor pressure at 20 C (68 F): 4.8 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, especially when in contact with water or metals such as aluminum, magnesium, and zinc.
2. Incompatibilities: Contact with chemically active metals such as potassium, powdered aluminum, magnesium, and zinc will cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving methyl chloride.
4. Special precautions: Methyl chloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not pertinent (gas)
2. Autoignition temperature: 632 C (1170 F)
3. Flammable limits in air, % by volume: Lower: 7.6; Upper: 19
4. Extinguishant: Stop flow of gas.

- **Warning properties**

May reports an odor threshold of 10 ppm. However, Patty states that methyl chloride has no odor or other warning properties, and Jacobs states that methyl chloride does not have adequate warning properties at higher concentrations.

Methyl chloride is not an eye irritant, according to Grant, even in concentrations which are "dangerously toxic."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methyl chloride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of methyl chloride. Each measurement should consist of a 5-minute sample or a series of consecutive samples totalling 5 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of methyl chloride on activated carbon, followed by desorption with methanol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl chloride may be used. An analytical method for methyl chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted

are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming wet with liquid methyl chloride or from becoming frozen from contact with vessels containing methyl chloride.
- Any clothing which becomes wet with liquid methyl chloride should be removed immediately and not reworn until the methyl chloride has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl chloride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of silicone resins, and tetramethyl lead; use as a methylating and chlorinating agent; use as a dewaxing agent in petroleum refining; use as a catalyst solvent in production of butyl rubber	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of a variety of other compounds; as an extractant for greases, oils, and resins	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use as a foaming agent in production of plastics; in the manufacture and application of pesticides, pharmaceuticals, and perfumes; as a propellant in aerosols; and use as a refrigerant	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquefied methyl chloride gets into the eyes, wash eyes immediately with large amounts of water. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquefied methyl chloride gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water if the methyl chloride has not already evaporated. If liquefied methyl chloride soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl chloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If methyl chloride is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas.

- Waste disposal method:

Methyl chloride may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR METHYL CHLORIDE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Chloroform

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3CCl_3
- Synonyms: 1,1,1-trichloroethane; 1,1,1-trichloroethane, stabilized
- Appearance and odor: Colorless liquid with a mild odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl chloroform is 350 parts of methyl chloroform per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1910 milligrams of methyl chloroform per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 350 ppm (1910 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for 1,1,1-Trichloroethane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl chloroform can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to methyl chloroform vapor may cause headache, dizziness, drowsiness, unconsciousness, irregular heart beat, and death. Methyl chloroform liquid splashed in the eyes may cause irritation.

2. Long-term Exposure: Prolonged or repeated skin contact with liquid methyl chloroform may cause irritation of the skin. Reproductive abnormalities have been noted in studies of animals exposed to high concentrations of methyl chloroform.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl chloroform.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl chloroform at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, and cardiovascular system should be stressed. The physician should be made aware of any adverse reproductive effects in workers exposed to methyl chloroform.

—Skin disease: Methyl chloroform can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: At high concentrations, methyl chloroform causes liver changes in animals, which justifies consideration of the possible consequences before exposing persons with impaired liver function.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of methyl chloroform might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

—Medical warning: Workers should be provided with information advising them of studies in which congenital abnormalities were found following exposure of animals to high concentrations of methyl chloro-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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form. The physician should be made aware of any reproductive abnormalities in workers.

*2. Periodic Medical Examination:*The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methyl chloroform vapor is a narcotic. Repeated exposure of animals to concentrations of 1000 to 10,000 ppm caused liver and lung changes in some species. In dogs, cardiac sensitization to epinephrine occurred at concentrations of 5000 to 10,000 ppm. A number of human fatalities related to industrial exposure in closed spaces have been reported. A 5-minute exposure to 5000 ppm can be expected to produce marked incoordination and anesthesia. Prolonged exposure at this concentration may cause coma and death. Exposure to concentrations in excess of 1000 ppm for 15 minutes, or 2000 ppm for 5 minutes, can be expected to produce a disturbance of equilibrium in the majority of adults. Above 1700 ppm, minor disturbances of equilibrium have been observed, with complaints of headache and lassitude. In controlled human exposures to 500 ppm no effects other than slight, transient eye irritation were noted; at 1000 ppm and above, mild eye irritation was experienced by all subjects, and some became dizzy. Following exposure, most of the compound is eliminated unchanged via the lungs within 48 hours. When placed into the rabbit eye, the liquid caused conjunctival irritation but no corneal damage. Dermatitis may result from repeated skin contact with the liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 133.4
2. Boiling point (760 mm Hg): 74 C (165 F)
3. Specific gravity (water = 1): 1.33
4. Vapor density (air = 1 at boiling point of methyl chloroform): 4.55
5. Melting point: −38 C (−36 F)
6. Vapor pressure at 20 C (68 F): 100 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.07
8. Evaporation rate (butyl acetate = 1): 12.8

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong caustics, strong oxidizers, and chemically active metals such as aluminum and magnesium powders, or sodium and potassium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving methyl chloroform.
4. Special precautions: Liquid methyl chloroform will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: None in normal test method.
2. Autoignition temperature: 500 C (932 F)
3. Flammable limits in air, % by volume: (At elevated temperature and pressure) Lower: 7; Upper: 16
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that the odor threshold of methyl chloroform may range from 20 to 100 ppm. Both May and Summer give 400 ppm as the odor threshold, however.
2. Eye Irritation Level: The *Hygienic Guide* states that "in controlled human exposures to 500 ppm no effects other than slight, transient eye irritation were noted, but at 1000 ppm and above, mild eye irritation was experienced by all subjects."
3. Evaluation of Warning Properties: Since the odor threshold of methyl chloroform is near or below the permissible exposure limit, and since eye irritation occurs at a concentration only twice the permissible exposure limit, methyl chloroform is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methyl chloroform. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl chloroform may be used. An analytical method for methyl chloroform is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl chloroform.
- Non-impervious clothing which becomes wet with liquid methyl chloroform should be removed promptly and not reworn until the methyl chloroform is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl chloroform may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl chloroform should be promptly washed or showered to remove any methyl chloroform.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl chloroform may occur and control methods which may be effective in each case:

Operation	Controls
Use as solvent in cold cleaning of metals, and plastics; in vapor degreasing; in ultrasonic cleaning; in dyeing and cleaning of fabrics and yarns	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in polymer manufacture; as primary and carrier solvent in spot cleaners, adhesives, shoe polishes, stain repellants, hair sprays, Mace, insecticides, resins, inks, lubricants, protective coatings, asphalt extraction, and waste water treatment; use in aerosol manufacture as pressure depressant	Process enclosure; local exhaust ventilation
Use as coolant and lubricant in cutting oils on metals; use during printed circuit boards production; liquid Drano production and photographic film processing	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl chloroform gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl chloroform gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If methyl chloroform soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl chloroform, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl chloroform has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl chloroform is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Methyl chloroform may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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- American Conference of Governmental Industrial Hygienists: "Methyl Chloroform," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYL CHLOROFORM

Condition	Minimum Respiratory Protection* Required Above 350 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methylcyclohexane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3C_6H_{11}$
- Synonyms: Cyclohexylmethane; hexahydrotoluene
- Appearance and odor: Colorless liquid with a faint, benzene-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylcyclohexane is 500 parts of methylcyclohexane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of methylcyclohexane per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for methylcyclohexane a Threshold Limit Value of 400 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylcyclohexane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to methylcyclohexane may cause light-headedness and drowsiness. It may also cause a slight irritation of the eyes, nose, and throat. At high concentrations, it may cause unconsciousness and death.
2. *Long-term Exposure:* Prolonged exposure to the liquid may cause irritation of the skin.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylcyclohexane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylcyclohexane at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylcyclohexane exposure.

—Skin disease: Methylcyclohexane is a skin defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methylcyclohexane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methylcyclohexane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylcyclohexane might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylcyclohexane vapor is a mild narcotic. Concentrations of 10,000 to 12,500 ppm were fatal to mice. Rabbits exposed to 3330 ppm for 300 hours showed minor evidence of liver and kidney injury, while 1200 ppm was innocuous for rabbits, and prolonged exposure at 370 ppm was harmless to monkeys. No toxic effects from industrial exposure have been reported. Prolonged

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or repeated skin contact may produce drying and irritation due to defatting action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 98
  2. Boiling point (760 mm Hg): 101 C (214 F)
  3. Specific gravity (water = 1): 0.77
  4. Vapor density (air = 1 at boiling point of methylcyclohexane): 3.4
  5. Melting point: −126 C (−196 F)
  6. Vapor pressure at 20 C (68 F): 37 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methylcyclohexane.
  4. Special precautions: Methylcyclohexane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −3.9 C (25 F) (closed cup)
  2. Autoignition temperature: 250 C (482 F)
  3. Flammable limits in air, % by volume: Lower: 1.2; Upper: 6.7
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Sax states that at the level of 500 ppm, methylcyclohexane "exhibits only a very faint odor."
  2. Irritation Levels: Sax states that "this material does not cause irritation to the eyes and nose."
  3. Evaluation of Warning Properties: At concentrations within two or three times the permissible exposure limit, methylcyclohexane can be detected through its odor. Therefore, for the purposes of this guideline, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methylcyclohexane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylcyclohexane may be used. An analytical method for methylcyclohexane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylcyclohexane.
- Clothing wet with liquid methylcyclohexane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylcyclohexane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylcyclohexane, the person performing the operation should be informed of methylcyclohexane's hazardous properties.
- Any clothing which becomes wet with liquid methylcyclohexane should be removed immediately and not reworn until the methylcyclohexane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylcyclohexane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylcyclohexane should be promptly washed or showered with soap or mild detergent and water to remove any methylcyclohexane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylcyclohexane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a diluent solvent for cellulose during spray application of lacquers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during wire- and textile-coating operations with resins and rubber	General dilution ventilation
Liberation during brush and hand application of synthetic varnishes, lacquers, and paints	General dilution ventilation; personal protective equipment
Use during manufacture of rotogravure inks	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent for oils, fats, waxes, and rubber; use as a diluent in resin molding; use as a degreasing agent	General dilution ventilation; personal protective equipment
Use in industrial organic synthesis in hydroreforming process	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methylcyclohexane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylcyclohexane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If methylcyclohexane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylcyclohexane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If methylcyclohexane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylcyclohexane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methylcyclohexane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Methylcyclohexane may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methylcyclohexane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYLCYCLOHEXANE

Condition	**Minimum Respiratory Protection* Required Above 500 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister. Any supplied-air respirator. Any self-contained breathing apparatus.
10,000 ppm or less	A gas mask with a front- or back-mounted organic vapor canister. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methylcyclohexanol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_7H_{14}O$
- Synonyms: Hexahydrocresols; mixture of 2-, 3-, and 4-methylcyclohexanols
- Appearance and odor: Straw-colored liquid with a weak coconut oil odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylcyclohexanol is 100 parts of methylcyclohexanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 470 milligrams of methylcyclohexanol per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for methylcyclohexanol a Threshold Limit Value of 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylcyclohexanol can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Headache and irritation of the eyes, nose, and throat may result from prolonged exposure to excessive concentrations of methylcyclohexanol. Prolonged or repeated contact of liquid methylcyclohexanol may cause a skin rash. In animal experiments methylcyclohexanol has caused drowsiness, unconsciousness, and mild liver and kidney damage.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylcyclohexanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylcyclohexanol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylcyclohexanol exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylcyclohexanol might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Methylcyclohexanol causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Methylcyclohexanol causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Methylcyclohexanol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Neurologic disorders: By analogy to effects observed in animals, methylcyclohexanol may adversely affect the nervous system.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylcyclohexanol vapor is a mild irritant of the eyes and mucous membranes in animals; high concentrations cause signs of narcosis. The oral LD50 in rats was approximately 2 g/kg; effects were signs of narcosis;

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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autopsy findings included congestive changes in several organs, including the liver and kidneys. Repeated daily application of large doses to the skin of rabbits caused skin irritation, weakness, tremor, narcosis, and death. Repeated daily exposure of rabbits to 503 ppm for 10 weeks caused conjunctivitis and lethargy; 230 ppm caused no effects; narcosis did not occur at the highest vapor concentration achievable at room temperature. In humans, headache and irritation of the eyes and upper respiratory tract may result from prolonged exposure to excessive concentrations. Prolonged or repeated contact of the liquid on the skin may cause dermatitis due to a defatting action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.2
2. Boiling point (760 mm Hg): 155 – 180 C (311 – 356 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of methylcyclohexanol): 3.9
5. Melting point: Less than −21 C (less than −6 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Slight
8. Evaporation rate (butyl acetate = 1): 0.02

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methylcyclohexanol.
4. Special precautions: Methylcyclohexanol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 65 C (149 F) (closed cup)
2. Autoignition temperature: 296 C (565 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that "methylcyclohexanol vapor in air can be detected and recognized by its odor when present to the extent of 500 ppm . . . ."
2. Eye Irritation Level: The *Handbook of Organic Industrial Solvents* states that eye irritation does not occur until concentrations reach 500 ppm.
3. Other Information: Patty states that 500 ppm is capable of causing upper respiratory tract irritation.
4. Evaluation of Warning Properties: Since the odor and irritation thresholds of methylcyclohexanol are not within three times the permissible exposure limit, methylcyclohexanol is treated like a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for methylcyclohexanol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylcyclohexanol.
- Clothing wet with methylcyclohexanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylcyclohexanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylcyclohexanol, the person performing the operation should be informed of methylcyclohexanol's hazardous properties.
- Non-impervious clothing which becomes contaminated with methylcyclohexanol should be removed promptly and not reworn until the methylcyclohexanol is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid methylcyclohexanol may contact the eyes.

SANITATION

- Skin that becomes contaminated with methylcyclohexanol should be promptly washed or showered with soap or mild detergent and water to remove any methylcyclohexanol.
- Employees who handle liquid methylcyclohexanol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylcyclohexanol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in lacquers, oils, gums, waxes, and resins	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an auxiliary solvent for dry cleaning soaps in soap manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use in textile industry as a blending agent in textile soaps; use as a degreaser; as an antioxidant in lubricants	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid methylcyclohexanol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid methylcyclohexanol gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid methylcyclohexanol soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylcyclohexanol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methylcyclohexanol has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylcyclohexanol is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and reclaimed or atomized in a suitable combustion chamber.

- Waste disposal methods:

Methylcyclohexanol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methylcyclohexanol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYLCYCLOHEXANOL

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for o-Methylcyclohexanone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_7H_{12}O$
- Synonyms: 2-Methylcyclohexanone
- Appearance and odor: Colorless liquid with a weak peppermint odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-methylcyclohexanone is 100 parts of o-methylcyclohexanone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 460 milligrams of o-methylcyclohexanone per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for o-methylcyclohexanone a Threshold Limit Value of 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

o-Methylcyclohexanone can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed.

- **Effects of overexposure**

There are no reported effects of human exposure to o-methylcyclohexanone. In animal experiments o-methylcyclohexanone has caused drowsiness, unconsciousness, irritation of the eyes, nose, and throat, and skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to o-methylcyclohexanone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to o-methylcyclohexanone at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from o-methylcyclohexanone exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of o-methylcyclohexanone might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although o-methylcyclohexanone is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although o-methylcyclohexanone is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: o-Methylcyclohexanone is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Neurologic disorders: By analogy to effects observed in animals, the nervous system may be adversely affected by o-methylcyclohexanone.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

o-Methylcyclohexanone vapor irritates the eyes and mucous membranes in animals; at high concentrations it

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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causes narcosis. Several species of animals exposed to 3500 ppm suffered marked irritation of the mucous membranes, became incoordinated after 15 minutes of exposure, and prostrate after 30 minutes. Repeated daily application to the skin of rabbits of large doses of the liquid caused irritation of the skin, tremors, narcosis, and death. Exposure of mice to 450 ppm for an unspecified time period resulted in irritation of the eyes and respiratory tract. Repeated or prolonged contact of the liquid with the skin may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 112.2
2. Boiling point (760 mm Hg): 165 C (329 F)
3. Specific gravity (water = 1): 0.93
4. Vapor density (air = 1 at boiling point of o-methylcyclohexanone): 3.9
5. Melting point: −14 C (6.8 F)
6. Vapor pressure at 20 C (68 F): 1 mm Hg (approximately)
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving o-methylcyclohexanone.
4. Special precautions: o-Methylcyclohexanone will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 47.8 C (118 F) (Closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of o-methylcyclohexanone.
2. Irritation Level: According to Patty, eye and respiratory irritation may occur below the permissible exposure limit.
3. Evaluation of Warning Properties: Through its irritant effects, o-methylcyclohexanone can be detected at the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for o-methylcyclohexanone is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid o-methylcyclohexanone.
- Clothing wet with o-methylcyclohexanone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of o-methylcyclohexanone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-methylcyclohexanone, the person performing the operation should be informed of o-methylcyclohexanone's hazardous properties.
- Non-impervious clothing which becomes contaminated with o-methylcyclohexanone should be removed

promptly and not reworn until the o-methylcyclohexanone is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid o-methylcyclohexanone may contact the eyes.

SANITATION

- Skin that becomes contaminated with o-methylcyclohexanone should be promptly washed or showered with soap or mild detergent and water to remove any o-methylcyclohexanone.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to o-methylcyclohexanone may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in plastic industry; manufacture of lacquers and varnishes; as a co-solvent with cyclohexanone	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in leather industry; use as a rust remover	Process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid o-methylcyclohexanone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid o-methylcyclohexanone gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid o-methylcyclohexanone soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of o-methylcyclohexanone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When o-methylcyclohexanone has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If o-methylcyclohexanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and reclaimed or atomized in a suitable combustion chamber. o-Methylcyclohexanone should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of o-methylcyclohexanone vapors are permitted.

- Waste disposal methods:

o-Methylcyclohexanone may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "o-Methylcyclohexanone," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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tration and Cutaneous Application," *Journal of Industrial Hygiene and Toxicology*, 25:199-214, 1943.

- Treon, J. F., et al.: "The Physiological Response of Rabbits to Cyclohexane, Methylcyclohexane, and Certain Derivatives of These Compounds. II. Inhalation," *Journal of Industrial Hygiene and Toxicology*, 25:323-347, 1943.

RESPIRATORY PROTECTION FOR o-METHYLCYCLOHEXANONE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methylene Bisphenyl Isocyanate (MDI)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $NCOC_6H_4CH_2\ C_6H_4NCO$
- Synonyms: MDI; 4,4-diphenylmethane diisocyanate; methylene bis (4-phenyl isocyanate); 4,4-diisocyantodiphenylmethane
- Appearance and odor: White to light-yellow flakes with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene bisphenyl isocyanate is a ceiling level of 0.02 part of methylene bisphenyl isocyanate per million parts of air (ppm). This may also be expressed as 0.2 milligram of methylene bisphenyl isocyanate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylene bisphenyl isocyanate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

*1. Short-term Exposure:*Exposure to methylene bisphenyl isocyanate may make a person allergic to it and produce wheezing, shortness of breath, and coughing. It may also cause irritation of the eyes and lungs, upset stomach, vomiting, possibly fever, stuffiness of the nose, sore throat, a feeling of tightness in the chest, cough, shortness of breath and wheezing. Such symptoms may be delayed up to eight hours after the person has been exposed.

2. Long-term Exposure: A person may become increasingly sensitive or allergic to methylene bisphenyl isocyanate. Chronic exposure to it may lead to permanent breathing or chest problems. Repeated or prolonged exposure of the skin to methylene bisphenyl isocyanate may cause a skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylene bisphenyl isocyanate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylene bisphenyl isocyanate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to methylene bisphenyl isocyanate would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Methylene bisphenyl isocyanate may cause lung damage in humans. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methylene bisphenyl isocyanate is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Methylene bisphenyl isocyanate (MDI) vapor is a potent respiratory sensitizer. It also is a strong irritant of the eyes, mucous membranes, and skin and can cause

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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pulmonary edema. Exposure of humans to high concentrations causes cough, dyspnea, increased secretions, and chest pain. Isocyanates cause pulmonary sensitization in susceptible individuals; should this occur, further exposure should be avoided, since extremely low levels of exposure may trigger an asthmatic episode; cross sensitization to unrelated materials probably does not occur. The liquid in contact with the eye may cause an irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 250.25
2. Boiling point (760 mm Hg): 172 C (341.6 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of methylene bisphenyl isocyanate): 8.6
5. Melting point: 37 C (98.6 F)
6. Vapor pressure at 20 C (68 F): 0.05 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 37.8 C (100 F)
2. Incompatibilities: Avoid contact with strong alkalies, acids, and alcohol.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving methylene bisphenyl isocyanate.
4. Special precautions: Liquid methylene bisphenyl isocyanate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 202 C (395.6 F) (open cup)
2. Autoignition temperature: 240 C (464 F)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Carbon dioxide, dry chemical, or inert gas. For large fires, water in the form of spray should be used.

- **Warning properties**

1; Odor Threshold: No quantitative information is available.

2; Irritation Levels: By analogy to TDI, which, according to Grant, causes irritation of the eyes and nose beginning at 0.05 ppm to 0.1 ppm, MDI is assumed to produce eye and nose irritation at the same levels.

3; Evaluation of Warning Properties: MDI is treated as a material with poor warning properties, for the purposes of this guideline. By analogy with TDI, MDI is assumed to produce eye and nose irritation within several times the permissible exposure limit, but the permissible exposure is a ceiling concentration.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene bisphenyl isocyanate. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

At the time of publication of this guideline, no measurement method for methylene bisphenyl isocyanate had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate, where skin contact may occur.
- If employees' clothing may have become contaminated with methylene bisphenyl isocyanate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with methylene bisphenyl isocyanate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylene bisphenyl isocyanate from

the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylene bisphenyl isocyanate, the person performing the operation should be informed of methylene bisphenyl isocyanate's hazardous properties.

- Non-impervious clothing which becomes contaminated with methylene bisphenyl isocyanate should be removed promptly and not reworn until the methylene bisphenyl isocyanate is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate contacting the eyes.

SANITATION

- Skin that becomes wet with methylene bisphenyl isocyanate should be promptly washed or showered with soap or mild detergent and water to remove any methylene bisphenyl isocyanate.
- Employees who handle solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylene bisphenyl isocyanate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during in place spraying of urethane foams	Local exhaust ventilation; respiratory protective equipment
Liberation during in place molding of urethane foams	Local exhaust ventilation; dilution ventilation
Liberation during application of polyisocyanate lacquer sealant finishes	Local exhaust ventilation; respiratory protective equipment
Liberation during shake-out and core knock-out operations at foundries using MDI-oil-base-no-bake binding systems	Local exhaust ventilation; respiratory protective equipment
Liberation during manufacture of lacquer	Process enclosure; local exhaust ventilation
Liberation during production of component chemicals for foam systems	Local exhaust ventilation; process enclosure
Liberation during casting of high-density polyurethane elastomers	Process enclosure; local exhaust ventilation
Liberation following combustion of urethane foams in fires or thermal decomposition to salvage metal inserts	Air-supply respiratory protective equipment or local exhaust ventilation
Liberation of unreacted vapor during cutting and fabricating of polyurethane foams	Local exhaust ventilation; respiratory protective equipment
Liberation during curing process; during flame lamination of fabrics	Process enclosure; local ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of methylene bisphenyl isocyanate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify some-

one else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylene bisphenyl isocyanate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Methylene bisphenyl isocyanate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR METHYLENE BISPHENYL ISOCYANATE (MDI)

Condition	**Minimum Respiratory Protection*** **Required Above 0.02 ppm**
Vapor or Particulate Concentration	
1 ppm (10 mg/m³) or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm (100 mg/m³) or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 ppm (100 mg/m³) or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methylene Chloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2Cl_2
- Synonyms: Dichloromethane; methylene dichloride
- Appearance and odor: Colorless liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene chloride is 500 parts of methylene chloride per million parts of air (ppm) averaged over an eight-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for 5 minutes in any two-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 500 ppm averaged over a 15-minute period. NIOSH further recommends that permissible levels of methylene chloride be reduced where carbon monoxide is present. The NIOSH Criteria Document for Methylene Chloride should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylene chloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Methylene chloride is an anesthetic. Inhaling the vapor may cause mental confusion, light-headedness, nausea, vomiting, and headache. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and death. High vapor concentrations may also cause irritation of the eyes and respiratory tract. Exposure to this chemical may make the symptoms of angina worse. Skin exposure to the liquid may cause irritation. If the liquid is held in contact with the skin, it may cause skin burns. Splashes of the liquid into the eyes may cause irritation.

2. Long-term Exposure: Prolonged or repeated exposure to methylene chloride may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylene chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylene chloride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, cardiovascular system, and blood should be stressed. Clinical impressions of the autonomic nervous system and pulmonary function should be made, with additional tests conducted where indicated.

—Skin disease: Methylene chloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver function test: Methylene chloride causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Methylene chloride causes kidney damage in animals and this justifies special considera-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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tion before exposing persons with impaired renal function.

—Cardiovascular disease: Because of reports of excessive carbon monoxide levels following exposure to methylene chloride, persons with cardiac disease may be at increased risk.

—A complete blood count: A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Carboxyhemoglobin values should also be determined periodically, and any level above 5% should prompt an investigation of the worker and his workplace.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methylene chloride vapor is a mild narcotic. Exposure of animals to 15,000 ppm for 7 hours was fatal. Animal experiments have shown that continuous exposure to 1,000 ppm can be lethal in 5 to 7 weeks for dogs and that fatty livers, icterus, pneumonia, and splenic atrophy developed in dogs. Cardiac arrhytmias attributed to sensitization of the myocardium have been observed following exposure to high concentrations of some chlorinated hydrocarbons, but dogs exposed to 10,000 and 20,000 ppm of methylene chloride did not show this phenomenon. In human experiments, inhalation of 500 to 1000 ppm for 1 to 2 hours resulted in lightheadedness; there was sustained elevation of carboxyhemoglobin level. High exposures have resulted in deaths in industrial situations. Lower but unknown concentrations have caused such symptoms as lightheadedness, weakness, nausea, and "drunken behavior," resulting in mistakes and accidental falls. Phosgene poisoning has been reported to occur in several cases where methylene chloride was used in the presence of an open fire. Liquid methylene chloride is irritating to the skin on repeated contact. Splashed in the eye, it is painfully irritating, but is not likely to cause serious injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 84.9
2. Boiling point (760 mm Hg): 39.8 C (104 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of methylene chloride): 2.9
5. Melting point: −97 C (−142 F)
6. Vapor pressure at 20 C (68 F): 350 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.32
8. Evaporation rate (butyl acetate = 1): 27.5

- **Reactivity**

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as aluminum or magnesium powder, sodium and potassium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving methylene chloride.
4. Special precautions: Liquid methylene chloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: None with normal test method
2. Autoignition temperature: 556 C (1033 F)
3. Flammable limits in air, % by volume: (at elevated temperatures) Lower: 12; Upper: 19
4. Extinguishant: Dry chemical, carbon dioxide, foam

- **Warning properties**

1. Odor Threshold: Different authors have reported varying odor thresholds for methylene chloride. Summer and May both report 150 ppm; Kirk-Othmer and Sax both report 25 to 50 ppm; Spector reports 320 ppm. Patty, however, states that since one can become adapted to the odor, it cannot be considered an adequate warning property.
2. Eye Irritation Level: Grant reports that methylene chloride "presents no particular hazard to the eyes." Kirk-Othmer, however, reports that "methylene chloride vapor is seriously damaging to the eyes." Sax agrees with Kirk-Othmer's statement.

The *Documentation of TLV's* states that irritation of the eyes has been observed in workers who had been exposed to concentrations up to 5000 ppm, but that neurasthenic disorders were found in 50% and digestive disturbances in 30% of the persons exposed.

3. Other Information: Gleason reports that methylene chloride may be "irritating to the respiratory tract and may produce pulmonary edema" but gives no quantitative information. The *Documentation of TLV's* reports that in one investigation, irritation of the respiratory passages was observed in workers who had been exposed to concentrations up to 5000 ppm.
4. Evaluation of Warning Properties: Since no detailed information is available relating the irritant effects of methylene chloride to air concentrations and since adaptation to the odor occurs, methylene chloride is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene chloride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of methylene chloride. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylene chloride may be used. An analytical method for methylene chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylene chloride.
- Non-impervious clothing which becomes wet with liquid methylene chloride should be removed promptly and not reworn until the methylene chloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylene chloride may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylene chloride should be promptly washed or showered with soap or mild detergent and water to remove any methylene chloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylene chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in paint and varnish removers; manufacture of aerosols; cold cleaning and ultrasonic cleaning; and as an extraction solvent for foods and furniture processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a cooling solvent in manufacture of cellulose acetate; in organic synthesis; and in plastics processing	Process enclosure; local exhaust ventilation
Use as a solvent in vapor degreasing of thermal switches and thermometers	Process enclosure; local exhaust ventilation
Use as a secondary refrigerant in air conditioning and scientific testing	General dilution ventilation; local exhaust ventilation; personal protective equipment

Operation	Controls
Use as an extraction solvent for edible fats, coca, butter, beer flavoring in hops, decaffeinated coffee, oleoresin manufacture, oils, waxes, perfumes, flavorings, and drugs	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for paints, lacquers, varnishes, enamels, adhesives, rubber cements, manufacture of printed circuit boards, as a carrier for pharmaceutical tablet coatings, shrink-fitting of synthetic rubber covers, and dyeing of synthetic fibers	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methylene chloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylene chloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water if the methylene chloride has not already evaporated. If methylene chloride soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylene chloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methylene chloride has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methylene chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

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RESPIRATORY PROTECTION FOR METHYLENE CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Formate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HCOOCH_3$
- Synonyms: Methyl methanoate; formic acid, methyl ester
- Appearance and odor: Colorless liquid with a pleasant odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl formate is 100 parts of methyl formate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 250 milligrams of methyl formate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl formate can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to methyl formate may cause irritation of the eyes, nose, throat, and lungs. It may also cause drowsiness and, at high levels, unconsciousness and death.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl formate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl formate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl formate exposure.

—Eye disease: Methyl formate is an eye irritant. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl formate might cause exacerbation of symptoms due to its irritant properties.

—Neurological disorders: By analogy to effects observed in animals and by effects observed in humans, persons with pre-existing neurological disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methyl formate vapor at high concentrations is an irritant of the eyes and respiratory tract; it also causes narcosis in animals. Exposure of guinea pigs to 10,000 ppm for 3 hours was fatal; effects were eye and nose irritation, incoordination, narcosis, and pulmonary edema. Workers exposed to the vapor of a solvent containing 30% methyl formate, in addition to ethyl formate, methyl acetate, and ethyl acetate, complained of irritation of mucous membranes, oppression in the chest, dyspnea, symptoms of central nervous system depression, and temporary visual disturbances; air concentrations were not determined. No short-term effects were noted from experimental human exposures to 1500 ppm for 1 minute.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60.1
2. Boiling point (760 mm Hg): 31.7 C (89 F)
3. Specific gravity (water = 1): 0.98
4. Vapor density (air = 1 at boiling point of methyl formate): 2.1
5. Melting point: −100 C (−148 F)
6. Vapor pressure at 20 C (68 F): 476 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 30
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as formic acid and carbon monoxide) may be released in a fire involving methyl formate.
4. Special precautions: Methyl formate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18.9 C (−2 F) (closed cup)
2. Autoignition temperature: 465 C (869 F)
3. Flammable limits in air, % by volume: Lower: 5.0; Upper: 23
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold of 2000 ppm for methyl formate. Browning, however, states that "men exposed for 1 minute to 1500 ppm of the vapour in air noticed the odour of methyl formate . . . ." Browning states that olfactory fatigue occurs, and thus odor may not be an effective warning of exposure to dangerous concentrations.
2. Eye Irritation Level: Grant states that the vapor of methyl formate "has been found to cause no eye irritation in experimental animals at a concentration of 1500 ppm in air, but does cause some irritation at 3500 ppm."
3. Other Information: According to Grant, methyl formate in high concentrations causes nasal irritation also, but quantitative information is not given.
4. Evaluation of Warning Properties: Since the thresholds of odor and of irritation are well above the permissible exposure limit, methyl formate is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for methyl formate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl formate.
- Clothing wet with liquid methyl formate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl formate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl formate, the person performing the operation should be informed of methyl formate's hazardous properties.
- Any clothing which becomes wet with liquid methyl formate should be removed immediately and not reworn until the methyl formate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl formate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl formate should be promptly washed or showered to remove any methyl formate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl formate may occur and control methods which may be effective in each case:

Operation	Controls
Use as insecticide and larvicide for fumigating dried fruits, nuts, tobacco, cereals, and infected clothing	Personal protective equipment
Use as a general industrial solvent for greases, fatty acids, cellulose acetate, collodion, and celluloid	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for production of sulfa drugs, perfumes, dyes, military poison gases, and embalming fluid	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of methyl formate	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid methyl formate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid methyl formate gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid methyl formate soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl formate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl formate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl formate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Methyl formate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of methyl formate vapors are permitted.

- Waste disposal method:

Methyl formate may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYL FORMATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3500 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.**
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for 5-Methyl-3-Heptanone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_8H_{16}O$
- Synonyms: Ethyl sec-amyl ketone; ethyl amyl ketone; amyl ethyl ketone
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 5-methyl-3-heptanone is 25 parts of 5-methyl-3-heptanone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 130 milligrams of 5-methyl-3-heptanone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

5-Methyl-3-heptanone can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: 5-Methyl-3-heptanone may irritate the eyes, nose, and throat, and may cause headache, and dizziness. At very high air concentrations, the vapor may cause unconsciousness in a short time.

2. Long-term Exposure: Prolonged or repeated skin contact may cause dryness and irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 5-methyl-3-heptanone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 5-methyl-3-heptanone at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 5-methyl-3-heptanone exposure.

—Kidney disease: Although 5-methyl-3-heptanone is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 5-methyl-3-heptanone might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although 5-methyl-3-heptanone is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: 5-Methyl-3-heptanone is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

There is local irritation of tissues by solvent effect of 5-methyl-3-heptanone on lipids. Central nervous system depression may occur on exposure to high concentrations, producing narcosis. No chronic effects are reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 128

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2. Boiling point (760 mm Hg): 159 C (318 F)

3. Specific gravity (water = 1): 0.82

4. Vapor density (air = 1 at boiling point of 5-methyl-3-heptanone): 4.4

5. Melting point: −57 C (−70 F)

6. Vapor pressure at 20 C (68 F): 2 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 0.26

8. Evaporation rate (butyl acetate = 1): 0.26

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving 5-methyl-3-heptanone.

4. Special precautions: None

- **Flammability**

1. Flash point: 43.3 C (110 F) (Tag closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Carbon dioxide, dry chemical, or foam

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* reports that Shell Chemical Corporation determined the odor threshold to be 6 ppm.

2. Irritation Levels: According to the *Documentation of TLV's*, "Shell Chemical Corporation presented the following observations in respect to sensory responses by unconditioned personnel during or following 5-minute exposures to the vapor: . . . 50% Threshold, eye irritation 50 ppm 50% Threshold, nose irritation 50 ppm"

The irritation of the nose and eyes is, according to the *Documentation of TLV's*, transient.

3. Evaluation of Warning Properties: Since 5-methyl-3-heptanone has an odor threshold which is lower than the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of 5-methyl-3-heptanone vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 5-methyl-3-heptanone may be used. An analytical method for 5-methyl-3-heptanone is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).
number PB 245 851).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to protect any area of the body which may come in contact with liquid 5-methyl-3-heptanone.
- Clothing wet with 5-methyl-3-heptanone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 5-methyl-3-heptanone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 5-methyl-3-heptanone, the person performing the operation should be informed of 5-methyl-3-heptanone's hazardous properties.
- Non-impervious clothing which becomes wet with 5-methyl-3-heptanone should be removed promptly and not reworn until the 5-methyl-3-heptanone is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 5-methyl-3-heptanone may contact the eyes.

SANITATION

- Skin that becomes wet with 5-methyl-3-heptanone should be promptly washed or showered to remove any 5-methyl-3-heptanone.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 5-methyl-3-heptanone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of resinous and lacquer surface coatings	Local exhaust ventilation; personal protective equipment
Liberation during subdivision of large quantities of ethyl amyl ketone or compounds containing it	General dilution ventilation; personal protective equipment
Use in preparation of perfumes	Local exhaust ventilation; personal protective equipment
Use as a specialized solvent in cleaning operations	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 5-methyl-3-heptanone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 5-methyl-3-heptanone gets on the skin, promptly flush the contaminated skin with water. If 5-methyl-3-heptanone soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is evidence of skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of 5-methyl-3-heptanone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 5-methyl-3-heptanone has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 5-methyl-3-heptanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. 5-Methyl-3-heptanone should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of 5-methyl-3-heptanone vapors are permitted.

- Waste disposal methods:

5-Methyl-3-heptanone may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR 5-METHYL-3-HEPTANONE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR MONOMETHYL HYDRAZINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about monomethyl hydrazine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** CH_6N_2
- **Structure:** CH_3NHNH_2
- **Synonyms:** Hydrazomethane, 1-methyl hydrazine, methyl hydrazine, MMH
- **Identifiers:** CAS 60-34-4; RTECS MV5600000; DOT 1244, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Colorless liquid with a strong ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46.09
2. Boiling point (at 760 mmHg): 87.5°C (189°F)
3. Specific gravity (water = 1): 0.874
4. Vapor density (air = 1 at boiling point of monomethyl hydrazine): 1.59
5. Melting point: -52.4°C (-61.6°F)
6. Vapor pressure: At 20°C (68°F): 36.0 mmHg; at 25°C (77°F), 49.6 mmHg
7. Soluble in water
8. Evaporation rate (butyl acetate = 1): 1.5
9. Saturation concentration in air (approximate) at 25°C (77°F): 6.5% (65,300 ppm)
10. Ionization potential: 7.67 eV

- **Reactivity**

Incompatibilities: Monomethyl hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.

Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving monomethyl hydrazine.

Caution: Monomethyl hydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -8.3°C (17°F) (closed cup)
2. Autoignition temperature: 194°C (382°F)
3. Flammable limits in air, % by volume: Lower, 2.5; upper, 92
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Monomethyl hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

1. Odor threshold: 1-3 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for monomethyl hydrazine is 0.2 parts of monomethyl hydrazine per million parts of air (ppm) [0.35 milligrams of monomethyl hydrazine per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that monomethyl hydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is

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0.04 ppm (0.08 mg/m³) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated monomethyl hydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value ceiling (TLV®-C), the concentration that should not be exceeded during any part of the working exposure, of 0.2 ppm (0.35 mg/m³) (Skin) (Table 1).

Table 1.—Occupational exposure limits for monomethyl hydrazine

	Exposure limits	
	ppm	mg/m³
OSHA PEL		
Ceiling (Skin)*	0.2	0.35
NIOSH REL (Ca)†		
Ceiling (120 min)	0.04	0.08
ACGIH TLV® (A2)§		
Ceiling (Skin)	0.2	0.35

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Monomethyl hydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute inhalation of monomethyl hydrazine by dogs caused respiratory irritation, pulmonary hemorrhage and edema, central nervous system stimulation, and convulsions; acute subcutaneous injection in dogs caused damage to the kidneys (including hemoglobinuria, hyaline droplet degeneration, and severe renal epithelial damage). Subchronic inhalation of monomethyl hydrazine by dogs, monkeys, rats, or mice produced nose and eye irritation, diarrhea, rapid respiration, deficient oxygenation of the blood (cyanosis), impaired muscular coordination (ataxia), tremors, convulsions, blood disorders (including significant hemolysis and hemolytic anemia), increased storage of iron in the body (hemosiderosis), and reduced bile flow (cholestasis). Chronic oral administration of monomethyl hydrazine to mice produced lung tumors; hamsters similarly exposed developed liver cancer.

- **Signs and symptoms of exposure**

Short-term (acute): Monomethyl hydrazine can cause irritation of the eyes and respiratory tract, nausea, diarrhea, and convulsions.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to monomethyl hydrazine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, liver, kidneys, and hematopoietic (blood-cell-forming), respiratory, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to monomethyl hydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver, kidneys, and hematopoietic and respiratory systems. The physician should obtain baseline values for liver function tests. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to monomethyl hydrazine.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to monomethyl hydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, liver, kidneys, and hematopoietic, respiratory, and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and lung function tests.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to monomethyl hydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of monomethyl hydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting monomethyl hydrazine vapors with sulfuric-acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure monomethyl hydrazine may also be used if available. A detailed sampling and analytical method for monomethyl hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with monomethyl hydrazine.

SANITATION

Clothing which is contaminated with monomethyl hydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of monomethyl hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of monomethyl hydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with monomethyl hydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle monomethyl hydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to monomethyl hydrazine may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to monomethyl hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If monomethyl hydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

Table 2.—Operations and methods of control for monomethyl hydrazine

Operations	Controls
During use in the preparation and handling of liquid rocket propellants; during use as a chemical intermediate for the synthesis of pesticides	Process enclosure, local exhaust ventilation, personal protective equipment
During use in polymer technology and in miscellaneous processes such as electroplating, etching, and photographic processing	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture and distribution of monomethyl hydrazine; during maintenance of storage containers	Process enclosure, local exhaust ventilation, personal protective equipment

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to monomethyl hydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If monomethyl hydrazine gets on the skin, wash it immediately with soap and water. If monomethyl hydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If monomethyl hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing monomethyl hydrazine may be flushed with water; the waste water may then be collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing monomethyl hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Monomethyl hydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for monomethyl hydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Iodide*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3I
- Synonyms: Iodomethane
- Appearance: Colorless liquid which turns yellow, red, and brown on exposure to light and moisture.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl iodide is 5 parts of methyl iodide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 28 milligrams of methyl iodide per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl iodide from 5 ppm to 2 ppm and has classified it as having a carcinogenic potential for man.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl iodide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Methyl iodide may cause nausea and vomiting, diarrhea, dizziness, slurred speech, visual disturbances, staggering, shaking, irritability, drowsiness, coma, and death. It may irritate the eyes and lungs. Contact with the liquid may cause irritation and blistering of the skin.

2. Long-term Exposure: Prolonged overexposure to methyl iodide may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl iodide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl iodide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methyl iodide vapor is an acute neurotoxin and possible pulmonary irritant. In mice, the LC50 for 57 minutes' exposure was 900 ppm; the minimum fatal dose with 24-hour exposure was 75 ppm. A chemical worker accidentally exposed to the vapor developed giddiness, diarrhea, sleepiness, and irritability, with recovery in a week; when re-exposed 3 months later, he experienced drowsiness, vomiting, pallor, incoordination, slurred speech, muscular twitching, oliguria, coma, and death. At autopsy there was bronchopneumonia and pulmonary hemorrhages, with accumulation of combined iodine in the brain. Experimental application of the liquid to human skin produced a stinging sensation and slight reddening in 10 minutes; after 6 hours' contact there was spreading erythema with later formation of vesicles. One report mentions the production of sarcomas in 15 of 24 rats of BD strain arising from the subcutaneous injection of methyl iodide in an oil solution, but the report is fragmentary.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 142
2. Boiling point (760 mm Hg): 42.5 C (108 F)
3. Specific gravity (water = 1): 2.3
4. Vapor density (air = 1 at boiling point of methyl iodide): 4.9
5. Melting point: −66 C (−87 F)
6. Vapor pressure at 20 C (68 F): 375 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 2
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, light, and moisture
2. Incompatibilities: Methyl iodide reacts with strong oxidizing agents.
3. Hazardous decomposition products: Toxic gases and vapors (such as iodine and hydrogen iodide) may be released when methyl iodide decomposes.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Although methyl iodide is known to have a sweet, ethereal odor, no quantitative data are available on the odor threshold. Methyl iodide is treated as a material with poor warning properties.

According to Grant, concentrations of methyl iodide of 4300 to 14,620 ppm caused immediate irritation of the eyes and lacrimation in mice, but 860 ppm for 10 minutes caused no irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl iodide vapors using an adsorption tube with subsequent desorption with toluene and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl iodide may be used. An analytical method for methyl iodide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl iodide.
- Non-impervious clothing which becomes contaminated with liquid methyl iodide should be removed immediately and not reworn until the methyl iodide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl iodide may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl iodide should be immediately washed or showered with soap or mild detergent and water to remove any methyl iodide.
- Employees who handle liquid methyl iodide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where liquid methyl iodide is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl iodide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a methylating agent in organic synthesis; use as a laboratory reagent; use in academic laboratory courses in organic chemistry	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an insecticidal fumigant on scale insects and beetles	Process enclosure; general dilution ventilation; personal protective equipment
Use in analytical chemistry laboratories (test for pyridine, evaluating type of sulfur linkage in vulcanized rubber)	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl iodide gets into the eyes, wash eyes promptly with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl iodide gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water. If methyl iodide soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl iodide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl iodide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl iodide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

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* SPECIAL NOTE

Methyl iodide appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR METHYL IODIDE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
800 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 800 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Isobutyl Carbinol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2CHCH_2CHOHCH_3$
- Synonyms: Methyl amyl alcohol; 4-methyl-2-pentanol; MIBC
- Appearance and odor: Colorless liquid with a mild odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl isobutyl carbinol is 25 parts of methyl isobutyl carbinol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of methyl isobutyl carbinol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl isobutyl carbinol can affect the body if it is swallowed, is inhaled, or comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to methyl isobutyl carbinol may cause eye and skin irritation. The overexposed person may also experience headache and drowsiness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl isobutyl carbinol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl isobutyl carbinol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl isobutyl carbinol exposure.

—Skin disease: Methyl isobutyl carbinol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methyl isobutyl carbinol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methyl isobutyl carbinol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Only limited observations of the effects of methyl isobutyl carbinol have been reported, but exposure of rats to 2000 ppm for 8 hours is fatal, while 1000 ppm is not. The most important effects of methyl isobutyl carbinol are narcosis and eye irritation. Unacclimated volunteer subjects exposed to 50 ppm vapor had eye irritation. Chronic systemic effects have not been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 102
  2. Boiling point (760 mm Hg): 132 C (269 F)
  3. Specific gravity (water = 1): 0.8

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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4. Vapor density (air = 1 at boiling point of methyl isobutyl carbinol): 3.5

5. Melting point: −90 C (−130 F)

6. Vapor pressure at 20 C (68 F): 3.8 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 1.5

8. Evaporation rate (butyl acetate = 1): 0.27

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl isobutyl carbinol.

4. Special precautions: Methyl isobutyl carbinol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 41 C (106 F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 5.5

4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* states that Silverman and associates observed that human subjects did not find the odor objectionable at 50 ppm.

2. Eye Irritation: According to the *Documentation of TLV's*, Silverman and associates found that human subjects experienced eye irritation at 50 ppm.

3. Evaluation of Warning Properties: Since eye irritation occurs at a level only twice the permissible exposure limit, this substance is considered to have good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl isobutyl carbinol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl isobutyl carbinol may be used. An analytical method for methyl isobutyl carbinol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, field, Virginia 22161, under the title "NIOSH Analyt-

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl isobutyl carbinol.
- Clothing wet with liquid methyl isobutyl carbinol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl isobutyl carbinol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl isobutyl carbinol, the person performing the operation should be informed of methyl isobutyl carbinol's hazardous properties.
- Non-impervious clothing which becomes wet with liquid methyl isobutyl carbinol should be removed promptly and not reworn until the methyl isobutyl carbinol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl isobutyl carbinol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl isobutyl carbinol should be promptly with soap or mild detergent and water washed or showered to remove any methyl isobutyl carbinol.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl isobutyl carbinol may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during application of nitrocellulose lacquers and other coatings; application of hot-spray lacquers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an extractant in dewaxing of mineral oils; use as a frother in froth flotation of various minerals, especially copper; use as an extractant in manufacture of antibiotics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during preparation of brake fluids; during preparation of lubricant additives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthesis of surfactants; use in preparation of lubricating oil additives	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl isobutyl carbinol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl isobutyl carbinol gets on the skin, promptly wash the contaminated skin with water. If methyl isobutyl carbinol soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl isobutyl carbinol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl isobutyl carbinol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl isobutyl carbinol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl isobutyl carbinol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl isobutyl carbinol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR METHYL ISOBUTYL CARBINOL

Condition	**Minimum Respiratory Protection* Required Above 25 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Isocyanate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3NCO
- Synonyms: None
- Appearance and odor: Colorless liquid with a sharp odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl isocyanate is 0.02 part of methyl isocyanate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.05 milligram of methyl isocyanate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl isocyanate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Inhalation of methyl isocyanate vapors may cause irritation of the eyes, nose, throat, and lungs. Cough, shortness of breath, increased phelgm and chest pain may be present. The liquid splashed in the eyes may cause permanent damage. The liquid splashed on the skin may cause irritation. Exposure to methyl isocyanate may cause a person to become allergic to it so that extremely low levels of exposure may cause an asthmatic attack.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl isocyanate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl isocyanate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to methyl isocyanate would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Methyl isocyanate causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methyl isocyanate is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Methyl isocyanate vapor is an intense lacrimator and irritates the eyes, mucous membranes, and skin. It can cause pulmonary irritation and sensitization. In rats exposed for 4 hours, the LC50 was 5 ppm; effects were injury to the lungs and subsequent pulmonary edema. Exposure of humans to high concentrations can cause cough, dyspnea, increased secretions, and chest pain. Isocyanates cause pulmonary sensitization in susceptible individuals; should this occur, further exposure should be avoided, since extremely low levels of expo-

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sure may trigger an asthmatic episode; cross sensitization to unrelated materials probably does not occur. Experimental exposure of four human subjects for 1 to 5 minutes caused the following effects: 0.4 ppm, no effects; 2 ppm, lacrimation, irritation of the nose and throat; 4 ppm, symptoms of irritation more marked; 21 ppm, unbearable irritation of eyes, nose, and throat. A cotton plug saturated with the liquid was applied to the ear of a rabbit for 30 minutes and caused erythema, edema, necrosis, and perforation; a few drops of the liquid on the ear of a rabbit caused destruction of tissue. The liquid in contact with the eye may cause permanent damage.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 57.1
2. Boiling point (760 mm Hg): 39 C (102 F)
3. Specific gravity (water = 1): 0.96
4. Vapor density (air = 1 at boiling point of methyl isocyanate): 2.0
5. Melting point: −80 C (−112 F)
6. Vapor pressure at 20 C (68 F): 348 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 6.7 (reacts slowly)
8. Evaporation rate (butyl acetate = 1): 26.8

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause methyl isocyanate to polymerize and burst container.
2. Incompatibilities: Contact with water causes formation of carbon dioxide and methylamine gases. The reaction is much more rapid in the presence of acids, alkalies, and amines. Contact with iron, tin, copper (or salts of these elements) and with certain other catalysts (such as triphenylarsenic oxide, triethylphosphine, and tributyltin oxide) may cause violent polymerization.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving methyl isocyanate.
4. Special precautions: Methyl isocyanate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −18 C (0 F) (open cup)
2. Autoignition temperature: 535 C (995 F)
3. Flammable limits in air, % by volume: Lower: 5.3; Upper: 26
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* states that humans exposed to 0.4 ppm methyl isocyanate for periods up to 5 minutes could not detect the odor. Even at a concentration of 2 ppm, the odor was not perceived.
2. Irritation Levels: At a concentration of 0.4 ppm, eye, nose, and throat irritation was not experienced by human subjects who were exposed for periods up to 5 minutes. The *Documentation of TLV's* states that "at 2 ppm no odor was detected, but the subjects experienced irritation and lacrimation. At 4 ppm the symptoms of irritation were more marked. Exposure was unbearable at 21 ppm."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of methyl isocyanate are not within 3 times the permissible exposure limit, for the purposes of this guideline, methyl isocyanate is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for methyl isocyanate had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid methyl isocyanate.

- Clothing wet with liquid methyl isocyanate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl isocyanate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl isocyanate, the person performing the operation should be informed of methyl isocyanate's hazardous properties.
- If employees' clothing has had any possibility of being contaminated with liquid methyl isocyanate, employees should change into uncontaminated clothing before leaving the work premises.
- Any clothing which becomes wet with and non-impervious clothing which becomes contaminated with liquid methyl isocyanate should be removed immediately and not reworn until the methyl isocyanate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid methyl isocyanate contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid methyl isocyanate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid methyl isocyanate should be immediately washed or showered to remove any methyl isocyanate.
- Employees who handle liquid methyl isocyanate should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl isocyanate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a cross-linking agent; additive to adhesives in polymer technology; use in organic synthesis	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid methyl isocyanate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid methyl isocyanate gets on the skin, immediately flush the contaminated skin with large amounts of water. If liquid methyl isocyanate soaks through the clothing, remove the clothing immediately and flush the skin with large amounts of water. If irritation persists after washing, get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of methyl isocyanate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid methyl isocyanate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl isocyanate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Methyl isocyanate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of methyl isocyanate vapors are permitted.

- Waste disposal method:

Methyl isocyanate may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR METHYL ISOCYANATE

Condition	Minimum Respiratory Protection* Required Above 0.02 ppm
Vapor Concentration	
0.2 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
20 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR METHYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about methyl mercaptan for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** CH_4S
- **Structure:** CH_3—SH
- **Synonyms:** Mercaptomethane, methanethiol, methyl sulfhydrate, thiomethyl alcohol
- **Identifiers:** CAS 74-93-1; RTECS PB4375000; DOT 1064, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with an odor like decaying cabbage

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 48.11
2. Boiling point (at 760 mmHg): 5.96°C (40.4°F)
3. Specific gravity (water = 1): 0.8665
4. Vapor density (air = 1 at boiling point of methyl mercaptan): 1.66
5. Melting point: -123°C (-190°F)
6. Vapor pressure at 20°C (68°F): 1,276 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 2.4
8. Ionization potential: 9.44 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents. Elevated temperature may generate high internal pressure and cause containers to burst.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving methyl mercaptan.
3. Caution: Liquid methyl mercaptan will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -18°C (0°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 3.9; upper, 21.8
3. Extinguishant: Carbon dioxide, dry chemicals, or alcohol foam
4. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 1 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, methyl mercaptan can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for methyl mercaptan is 10 parts of methyl mercaptan per million parts of air (ppm) [20 milligrams of methyl mercaptan per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.5 ppm (1.0 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1 mg/m^3) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for methyl mercaptan

	Exposure limits	
	ppm	mg/m^3
OSHA PEL ceiling	10	20
NIOSH REL ceiling (15 min)	0.5	1.0
ACGIH TLV® TWA	0.5	1.0

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HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl mercaptan may cause adverse health effects following exposure via inhalation or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of methyl mercaptan by rats and mice caused restlessness, increased respiration, muscular weakness progressing to paralysis, convulsions, respiratory depression, deficient oxygenation of the blood (cyanosis), and death due to respiratory paralysis. Subchronic inhalation of methyl mercaptan by monkeys, rats, and mice caused altered blood chemistries in all three species, pulmonary edema in monkeys, and persistent hepatitis and cellular changes of the liver, lungs, and kidneys in mice.
2. *Effects on humans:* An accidental industrial exposure of a worker to methyl mercaptan caused elevated blood pressure, severe hemolytic anemia, methemoglobinemia, deep coma, and death due to pulmonary embolus 28 days following exposure.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to methyl mercaptan can cause headache, dizziness, staggered gait, nausea, vomiting, pulmonary irritation, expiratory wheezing, rapid heart beat (tachycardia), rigidity of the arms and legs, bluish discoloration of the skin and mucous membranes (cyanosis), and irritation of the eyes and mucous membranes.
2. *Long-term (chronic):* Low-level exposure to methyl mercaptan can cause dermatitis.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to methyl mercaptan, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to methyl mercaptan at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin and respiratory system.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to methyl mercaptan. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of methyl mercaptan. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

There are no NIOSH-validated sampling and analytical methods for methyl mercaptan. Direct reading devices calibrated to measure methyl mercaptan may be used if available.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with methyl mercaptan.

Workers should be provided with and required to use splash-proof safety goggles where liquid methyl mercaptan may come in contact with the eyes.

SANITATION

Clothing which is contaminated with liquid methyl mercaptan should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of methyl mercaptan's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with methyl mercaptan should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle methyl mercaptan should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to methyl mercaptan may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for methyl mercaptan

Operations	Controls
During use in the manufacture and processing of methyl mercaptan and methionine; during use as a catalyst or activator; during use in wood processing	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in the synthesis of chemical intermediates for the manufacture of resins, plastics, insecticides, and pressure-sensitive and oil-resistant adhesives	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as an odorant and warning agent in natural gas; during use in jet fuels; during the cleaning and maintenance of storage containers	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to methyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If methyl mercaptan gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to methyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If methyl mercaptan gets on the skin, wash it immediately with soap and water. If methyl mercaptan penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If methyl mercaptan is spilled or leaked, the following steps should be taken:

1. If methyl mercaptan is in the gaseous form, stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing methyl mercaptan, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood duct work is free from methyl mercaptan vapors. Burn the paper in a suitable location away from combustible material.
5. Large quantities of liquids containing methyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Methyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing methyl mercaptan may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for methyl mercaptan

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator Any self-contained breathing apparatus Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 12.5 ppm	Any supplied-air respirator operated in a continuous flow mode Any powered air-purifying respirator with organic vapor cartridge(s)
Less than or equal to 25 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 400 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 400 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 ppm (1.0 mg/m^3) (ceiling).

Occupational Health Guideline for Methyl Methacrylate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_2=C(CH_3)COOCH_3$
- Synonyms: Methacrylic acid, methyl ester
- Appearance and odor: Colorless liquid with an acrid, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl methacrylate is 100 parts of methyl methacrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 410 milligrams of methyl methacrylate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl methacrylate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to methyl methacrylate may cause irritation of the nose, throat, skin, and eyes. It may also cause drowsiness and, at very high levels, perhaps unconsciousness.

2. *Long-term Exposure:* Prolonged exposure may cause a skin rash.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl methacrylate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl methacrylate at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl methacrylate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl methacrylate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl methacrylate can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although methyl methacrylate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although methyl methacrylate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The main toxic effect of methyl methacrylate is irritation of the respiratory tract by exposure to the vapor of the monomer. Rabbits exposed to 13,500 ppm for 3 hours died. Dust generated from the solid polymer is also irritating. Application to the eyes of rabbits caused irritation requiring several days for recovery. Dental technicians molding the polymer by hand developed dermatitis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): 100 C (212 F)
3. Specific gravity (water = 1): 0.95
4. Vapor density (air = 1 at boiling point of methyl methacrylate): 3.6
5. Melting point: −48 C (−54 F)
6. Vapor pressure at 20 C (68 F): 35 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): 3.1

- **Reactivity**

1. Conditions contributing to instability: Heat/and or lack of appropriate inhibitor concentration can cause methyl methacrylate to polymerize violently and burst container.
2. Incompatibilities: Contact with nitrates, oxidizing materials, including peroxides and other initiators of polymerization, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl methacrylate.
4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.

- **Flammability**

1. Flash point: 10 C (50 F) (closed cup)
2. Autoignition temperature: 421 C (790 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.2
4. Extinguishant: Dry chemical, foam, carbon dioxide

- Warning properties

1. Odor Threshold: May reports an odor threshold for methyl methacrylate of 0.21 ppm.
2. Eye Irritation Level: According to Grant, "on application to rabbit eyes it (methyl methacrylate) has caused irritation requiring several days for recovery. The TLV is recommended "to protect against discomfort from irritation."
3. Other Information: According to the *Documentation of TLV's*, some "investigators noted irritation at 170 to 250 ppm, but workers tolerated without complaint levels approximating 200 ppm . . . . It was the opinion of men in the field that 100 ppm could be tolerated continuously for 8 hours without discomfort."
4. Evaluation of Warning Properties: Since its odor threshold is below the permissible exposure limit, and since irritation occurs within 3 times the permissible exposure limit, methyl methacrylate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methyl methacrylate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl methacrylate may be used. An analytical method for methyl methacrylate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl methacrylate.
- Clothing wet with liquid methyl methacrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

methyl methacrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl methacrylate, the person performing the operation should be informed of methyl methacrylate's hazardous properties.

- Any clothing which becomes wet with liquid methyl methacrylate should be removed immediately and not reworn until the methyl methacrylate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl methacrylate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl methacrylate should be promptly washed or showered with soap or mild detergent and water to remove any methyl methacrylate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl methacrylate may occur and control methods which may be effective in each case:

Operation	Controls
Use during casting of acrylic sheets	Local exhaust ventilation; personal protective equipment
Use during molding of acrylic sheets or polymethacrylate powders	Local exhaust ventilation; general dilution ventilation
Use during spray application of unsaturated polyester resins (surface coatings or structural components); use during brush or roller applications of unsaturated polyester resins (surface coatings or structural components)	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of methyl methacrylate resins for surface coatings; during polymerization to produce molding and extruding powders	Process enclosure; general dilution ventilation
Liberation during production of synthetic fibers; during manufacture of unsaturated polyester resins	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during dye molding of articles from polyester resins; during production of emulsion polymers for use in adhesives, sealants, fabrics, sizes, leather finishes, paper coatings, polishes, etc.; during machining of articles from resins (acrylic plastics)	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If methyl methacrylate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methyl methacrylate gets on the skin, promptly flush the contaminated skin with water. If methyl methacrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl methacrylate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When methyl methacrylate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If methyl methacrylate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl methacrylate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl methacrylate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYL METHACRYLATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for alpha-Methyl Styrene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5C(CH_3)=CH_2$ or C_9H_{10}
- Synonyms: 1-Methyl-1-phenylethylene; AMS
- Appearance and odor: Colorless liquid with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for alpha-methyl styrene is a ceiling level of 100 parts of alpha-methyl styrene per million parts of air (ppm). This may also be expressed as 480 milligrams of alpha-methyl styrene per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for alpha-methyl styrene from 100 ppm to 50 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

alpha-Methyl styrene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: alpha-Methyl styrene may cause irritation of the eyes, nose, and throat. The overexposed person may experience drowsiness.

2. Long-term Exposure: Prolonged exposure may produce irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to alpha-methyl styrene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to alpha-methyl styrene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from alpha-methyl styrene exposure.

—Skin disease: alpha-Methyl styrene can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of alpha-methyl styrene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Kidney disease: Although alpha-methyl styrene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although alpha-methyl styrene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Overexposure to alpha-methyl styrene causes slight irritation of the eyes, upper respiratory tract, and skin. With prolonged and repeated contact, there may be depression of the central nervous system.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 118
  2. Boiling point (760 mm Hg): 165 C (329 F)
  3. Specific gravity (water = 1): 0.92
  4. Vapor density (air = 1 at boiling point of alpha-methyl styrene): 4.1
  5. Melting point: −23 C (−9 F)
  6. Vapor pressure at 20 C (68 F): 1.9 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Less than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with oxidizing agents (including peroxides and halogens) may cause fires and explosions. Also, avoid contact with catalysts for vinyl polymerization and catalysts for ionic polymerization, such as aluminum or iron chloride.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving alpha-methyl styrene.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 54 C (129 F) (closed cup)
  2. Autoignition temperature: 574 C (1066 F)
  3. Flammable limits in air, % by volume: Lower: 1.9; Upper: 6.1
  4. Extinguishant: Carbon dioxide, dry chemical, or foam.
- **Warning properties**
  1. Odor Threshold: According to the *Documentation of TLV's*, "four human subjects exposed to a concentration of 200 ppm of alpha-methyl styrene reported definite unpleasant odor . . . after two minutes." This concentration is not necessarily the odor threshold.
  2. Eye Irritation Level: The *Documentation of TLV's* also notes that at 200 ppm human subjects experienced eye irritation. This concentration is not necessarily the threshold of eye irritation.
  3. Evaluation of Warning Properties: alpha-Methyl styrene can be detected at a concentration less than twice the permissible exposure limit. Even though the permissible exposure limit is a ceiling concentration, alpha-methyl styrene is still treated as a material with adequate warning properties, since the ceiling appears to have been established to avoid irritant effects. The *Documentation of TLV's* gives the following quote of Dow Chemical Company: "We suggest, therefore, an Industrial Hygiene Standard of 200 ppm based on toxicity. For engineering purposes, we suggest that the vapor concentration be controlled to 100 ppm alpha-methyl styrene in order to minimize complaints of exposed persons."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of alpha-methyl styrene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of alpha-methyl styrene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure alpha-methyl styrene may be used. An analytical method for alpha-methyl styrene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid alpha-methyl styrene.
- Clothing wet with liquid alpha-methyl styrene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

alpha-methyl styrene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the alpha-methyl styrene, the person performing the operation should be informed of alpha-methyl styrene's hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid alpha-methyl styrene should be removed promptly and not reworn until the alpha-methyl styrene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid alpha-methyl styrene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid alpha-methyl styrene should be promptly washed or showered with soap or mild detergent and water to remove any alpha-methyl styrene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to alpha-methyl styrene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of styrene-butadiene rubber	General dilution ventilation
Liberation during spray application of specialized alpha-methyl-styrene-polyester surface coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during manufacture of high-impact acrylonitrile-butadiene-styrene plastics; during manufacture of specialized alpha-methyl-styrene-polyester and alkyd surface coating resins; during manufacture of certain plasticizers in varnishes, adhesives, and plastics; during manufacture of carbolic acid with cumene peroxidation process	General dilution ventilation; local exhaust ventilation
Liberation during brush application of specialized surface coatings	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If alpha-methyl styrene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If alpha-methyl styrene gets on the skin, promptly flush the contaminated skin with water. If alpha-methyl styrene soaks through the clothing, remove the clothing immediately and flush the skin with water When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of alpha-methyl styrene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If alpha-methyl styrene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If alpha-methyl styrene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid. Liquid alpha-methyl styrene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

alpha-Methyl styrene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary

landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid.

REFERENCES

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RESPIRATORY PROTECTION FOR ALPHA-METHYL STYRENE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Mica

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Muscovite (most important) is: $K_2Al_4(Al_2Si_6O_{20})(OH)_4$ (typical)
- Synonyms: Muscovite; amber mica; roscoelite; lepidolite; phlogopite; biotite; zinnwaldite; fluorophlogopite
- Appearance and odor: Colorless, odorless flakes or sheets containing less than 1% quartz (free crystalline silica).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mica is 20 million particles of mica per cubic foot of air (mppcf) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mica can affect the body if it is inhaled.

- **Effects of overexposure**

Exposure to mica dust over a period of years may cause scarring of the lungs. The symptoms which may occur with this condition are cough, shortness of breath, weakness, and weight loss.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to mica.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to mica at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Mica causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Mica causes pneumoconiosis. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Mica dust causes pneumoconiosis. In a study of 57 workers exposed to mica dust, 5 of the 6 workers exposed more than 10 years to concentrations in excess of 25 mppcf had pneumoconiosis. The most characteristic finding by chest x-ray was fine granulation of uneven density; there was a tendency to a coalescence of shadows in some cases. The symptoms most frequently reported were chronic cough and dyspnea; complaints of weakness and weight loss were less frequent.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Formula weight (muscovite): 797
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.6– 3.2
  4. Vapor density (air = 1 at boiling point of mica): Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20 C (68 F): Essentially zero

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Mica is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for mica had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to mica may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from open and underground mining operations	General dilution ventilation; local exhaust ventilation; dust collection; process enclosure; personal protective equipment; wet drilling
Use in manufacture of electrical insulation for low thermal conductivity and high dielectric strength	General dilution ventilation; local exhaust ventilation; dust collection; wet methods; personal protective equipment
Use in manufacture of asphalt shingles and roll roofing	General dilution ventilation; local exhaust ventilation; dust collection; process enclosure; personal protective equipment
Use in manufacture of paint, wall paper, and bituminized cardboard	General dilution ventilation; local exhaust ventilation; dust collection; wet methods; personal protective equipment
Use in manufacture of molded rubber products; plastics; special greases; absorbent of well drilling muds	General dilution ventilation; local exhaust ventilation; dust collection; personal protective equipment
Use in fabrication of windows and diaphragms	Process enclosure

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If mica gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Breathing**

If a person breathes in large amounts of mica, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If mica is spilled or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a sanitary landfill.

- Waste disposal method:

Mica may be disposed of in a sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR MICA

Condition	Minimum Respiratory Protection* Required Above 20 mppcf
Particulate Concentration	
100 mppcf or less	Any dust respirator.
200 mppcf or less	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
1000 mppcf or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 mppcf or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 10,000 mppcf or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Molybdenum and Insoluble Molybdenum

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all molybdenum and insoluble molybdenum compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic molybdenum

- Formula: Mo
- Synonyms: None
- Appearance: Silvery white metal or gray-black powder.

Molybdenum disulfide

- Formula: MoS_2
- Synonyms: Molybdenite
- Appearance and odor: Shiny gray, odorless plates.

Lead molybdate

- Formula: $PbMoO_4$
- Synonyms: Sulfenite
- Appearance and odor: Colorless to pale yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for molybdenum and insoluble molybdenum compounds is 15 milligrams of molybdenum and insoluble molybdenum compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for molybdenum and insoluble molybdenum compounds a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Molybdenum and insoluble molybdenum compounds can affect the body if they are inhaled or if they come in contact with the eyes. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Molybdenum trioxide has caused irritation of the eyes, nose, and throat, weight loss, and digestive disturbances in animals.

2. Long-term Exposure: Not known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to molybdenum and insoluble molybdenum compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to molybdenum and insoluble molybdenum compounds at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from molybdenum and insoluble molybdenum compounds exposure.

—Kidney disease: Fume from arcing molybdenum metal causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Chronic respiratory disease: Fume from arcing molybdenum metal causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of insoluble molybdenum compounds might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Fume from arcing molybdenum metal causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Molybdenum and its insoluble compounds, which include molybdenum disulfide, calcium molybdate, and many of the oxides and halides, have a low toxicity; however, molybdenum trioxide irritates the eyes and mucous membranes. Guinea pigs repeatedly exposed to molybdenum trioxide dust at a concentration of 200 mg molybdenum/m^3 for 1 hour daily developed nasal irritation, diarrhea, weight loss, and incoordination. In guinea pigs exposed to fume from arcing molybdenum metal, there were some deaths at 190 mg/m^3 but minimal effects at 53 mg/m^3; autopsy revealed bronchial and alveolar irritation with moderate fatty changes in the liver and kidneys. Animals receiving daily oral doses of up to 500 mg molybdenum per day in the form of molybdenum trioxide or calcium molybdate showed anorexia, listlessness, and weight loss. The metabolism of molybdenum is closely associated with that of copper; molybdenum toxicity to animals can be alleviated by the administration of copper. While molybdenum is essential to the action of certain enzymes, higher molybdenum levels may inhibit the action of these enzymes. High intake of molybdenum in rats resulted in a substantial reduction in activity of sulfide oxidase in the liver. The reduced activity of this enzyme leads to accumulation of sulfide in the tissues and subsequent formation of highly undissociated copper sulfide, thus removing copper from metabolic activity. This is a probable explanation for the induction of copper deficiency by molybdate. High dietary intake of molybdenum has been reported to be associated with a gout-like disease and high blood uric acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Metallic molybdenum**

1. Molecular weight: 95.94
2. Boiling point (760 mm Hg): 5,560 C (10,040 F)
3. Specific gravity (water = 1): 10.22
4. Vapor density (air = 1 at boiling point of metallic molybdenum): Not applicable
5. Melting point: 2,610 C (4,730 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Molybdenum disulfide**

1. Molecular weight: 160.1
2. Boiling point (760 mm Hg): Oxidizes above 315 C (599 F)
3. Specific gravity (water = 1): 4.7
4. Vapor density (air = 1 at boiling point of molybdenum disulfide): Not applicable
5. Melting point: 1370 C (2498 F) (oxidizes above 315 C (599 F))
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Lead Molybdate**

1. Molecular weight: 367.1
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 6.8
4. Vapor density (air = 1 at boiling point of lead molybdate): Not applicable
5. Melting point: 1066 C (1950 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.000012
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of finely divided molybdenite with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as molybdenum oxide fume, sulfur dioxide gas, and carbon monoxide) may be released when insoluble molybdenum compounds decompose.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: Molybdenum: 360 C (680 F) (layer); 720 C (1328 F) (cloud); Molybdenite: 290 C (554 F) (layer); 570 C (1058 F) (cloud)
3. Minimum explosive concentration: Data not available
4. Extinguishant: Molybdenum and molybdenum disulfide: Dry sand, dry dolomite, dry graphite

- **Warning properties**

None of the insoluble compounds of molybdenum are known to be significant eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of molybdenum and insoluble molybdenum compounds on a filter, followed by chemical treatment, and atomic absorption spectrophotometric analysis. An analytical method for molybdenum and insoluble molybdenum compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

- Eating and smoking should not be permitted in areas where solids containing molybdenum and insoluble molybdenum compounds are handled, processed, or stored.
- Employees who handle solids or liquids containing insoluble molybdenum compounds should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to molybdenum and insoluble molybdenum compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining and processing of ore; from grinding and other abrasive treatment of metal or alloys for use in electrical contacts, spark plugs, x-ray tubes, grids for radio tubes, missle and aircraft parts, and iron/steel alloys	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as lubricants in greases, oil dispersions, resin-bonded films, and dry powders; as catalysts in petroleum refining and chemical processing	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in pigment mixture for labelling glass bottles, for printing inks, for paints, and for plastics; as reagents in analytical chemistry laboratories	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in powder as chemical intermediates; use in molybdic acid; use as alloying agents in production of iron/steel	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as catalysts in organic synthesis in medicinals, in decorative and protective coatings for metal, and as feed additives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during temperature application as protective coatings for electrical resistors and engine parts, and as catalysts	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chemical intermediates and plating agents for mirrors; use in metal brazing and in manufacture of cutting tools	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

Liberation during use as solid lubricants	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation as catalysts in manufacture of propylene oxide	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical laboratory	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of molybdenum and insoluble molybdenum compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When molybdenum and insoluble molybdenum compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If molybdenum and insoluble molybdenum compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation, or for disposal in a secured sanitary landfill. Liquid containing insoluble molybdenum compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Molybdenum and insoluble molybdenum compounds may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Molybdenum as Mo," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR MOLYBDENUM AND INSOLUBLE MOLYBDENUM COMPOUNDS (AS MOLYBDENUM)

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Dust or Mist Concentration	
75 mg/m³ or less	Any dust and mist respirator, except single-use.
150 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
150 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7,500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7,500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Molybdenum Compounds (as Molybdenum)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble molybdenum compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION—Molybdenum trioxide

- Formula: MoO_3
- Synonyms: Molybdenum anhydride; molybdic oxide
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION—Ammonium molybdate

- Formula: $(NH_4)_2MoO_4$
- Synonyms: 85% molybdic acid
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION—Ammonium paramolybdate

- Formula: $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$
- Synonyms: None
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION—Calcium molybdate

- Formula: $CaMoO_4$
- Synonyms: None
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION—Sodium molybdate, dihydrate

- Formula: $Na_2MoO_4{\cdot}2H_2O$
- Synonyms: Sodium molybdate
- Appearance: White crystalline powder.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble molybdenum compounds is 5 milligrams of soluble molybdenum compounds (as molybdenum) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble molybdenum compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They might also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble molybdenum compounds have caused loss of appetite, incoordination, and irritation of eyes, nose, and throat, difficulty in breathing, anemia, and colic in animals.

2. Long-term Exposure: Animal data suggest that repeated exposure to soluble molybdenum compounds might be associated with gout.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble molybdenum compounds.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble molybdenum compounds at potentially hazardous levels:

1. Initial Medical Screening: Routine medical histories and physical examinations are not considered necessary. However, the employer should screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble molybdenum compounds exposure. Only those giving a positive history of these conditions should be referred for further medical examinations.

—Kidney disease: Although soluble molybdenum compounds are not known as kidney toxins in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of soluble molybdenum compounds might cause exacerbation of symptoms due to their irritant properties.

—Blood disease: Soluble molybdenum compounds cause anemia in animals. Persons with pre-existing blood disorders may be more susceptible to the effects of these agents.

—Gout: Soluble molybdenum compounds may cause gout. Persons with pre-existing conditions may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Routine periodic examinations are not considered necessary. However, anyone developing the above listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Soluble molybdenum compounds have a low toxicity but may cause anemia and deformities of the forelegs when fed to rabbits in high doses. In rats, the approximate oral LD50 for daily repeated doses of ammonium molybdate was 333 mg molybdenum/g/day; sodium molybdate was fatal to rabbits within a few weeks at a dietary level of 0.1%. In rats and guinea pigs, oral doses of 1.2 g/kg ammonium molybdate caused anorexia, colic, trembling, incoordination, and dyspnea; anemia and deformity of the forelegs occurred in rabbits. Exposure of mice for 1 hour to a high concentration of the dust of ammonium molybdate caused a transitory irritation of mucous membranes. While molybdenum is essential to the action of certain enzymes, higher molybdenum levels may inhibit the action of other enzymes. High intake of molybdenum in rats resulted in a substantial reduction in activity of sulfide oxidase in the liver. The reduced activity of this enzyme leads to accumulation of sulfide in the tissues and subsequent formation of highly undissociated copper sulfide, thus removing copper from metabolic activity. This is a probable explanation for the induction of copper deficiency by molybdate. There have been no reports of systemic effects from industrial exposure., A study from the Ankavan Province of Russia, where dietary molybdenum intake ranges from 10 to 15 mg per day due to high natural levels, has shown elevated blood xanthine oxidase activity and increased uric acid concentrations in blood of residents compared with controls living in an area with lower molybdenum exposure. A high percentage (31%) of the population examined from the Ankavan Province were diagnosed as having a gout-like disease.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Molybdic trioxide**

1. Molecular weight: 144
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.7
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: 795 C (1463 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.5
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Ammonium molybdate**

1. Molecular weight: 196
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.3
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Soluble, decomposes
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Ammonium paramolybdate**

1. Molecular weight: 1238
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.5
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 43
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Calcium molybdate**

1. Molecular weight: 200
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.35
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: 695 C (1283 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.01
8. Evaporation rate (butyl acetate = 1): Not applica-

ble

- **Physical data—Sodium molybdate, dihydrate**

1. Molecular weight: 241.95
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 3.28
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Loses its water at 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Data not available
7. Solubility in water, g/100 g water at 0 C (32 F): 56.2
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Ammonium molybdate and ammonium paramolybdate decompose above 360 C (680 F). Other are stable.
2. Incompatibilities: Contact with alkali metals such as sodium and potassium or with molten magnesium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia and carbon monoxide) may be released when some soluble molybdenum compounds decompose.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

According to Patty, "exposure to molybdenum oxide is irritating to eyes . . .," but he gives no quantitative information concerning the concentrations necessary. Examples of molybdenum compounds which cause eye irritation are: compounds containing nitrate, acetate, chloride, trioxide, and molybdate.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of soluble molybdenum compounds on a filter, followed by leaching-off of analyte with hot water and atomic absorption spectrophotometric analysis. An analytical method for soluble molybdenum compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with soluble molybdenum compounds or liquids containing soluble molybdenum compounds.
- Non-impervious clothing which becomes contaminated with soluble molybdenum compounds should be removed promptly and not reworn until the soluble molybdenum compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble molybdenum compounds or liquids containing soluble molybdenum compounds may contact the eyes.

SANITATION

- Skin that becomes contaminated with soluble molybdenum compounds should be promptly washed or showered with soap or mild detergent and water to remove any soluble molybdenum compounds.
- Eating and smoking should not be permitted in areas where soluble molybdenum compounds are handled, processed, or stored.
- Employees who handle soluble molybdenum compounds or liquids containing soluble molybdenum compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble molybdenum compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during rolling of hot billets in processing molybdenum steel; for use as electrodes; during welding operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chemical reagent for laboratory analyses; in petroleum refining and chemical processing; as an intermediate in the manufacture of corrosion inhibitors; use as coloring agents for enamels and ceramic glazes; agricultural chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in electroplating process; use in formulation of corrosion inhibitors for aqueous systems; pigments for paints, lacquers, and coloring animal fibers and hair	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in enamel processes for adherence of vitreous coatings to ceramics and metal; use in leather and skin tanning	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chlorination catalysts; in fire-retardant resins; as a brazing flux and as an intermediate for organo-metallic compounds; use in photography; ion exchange processes and formulation of plastics and adhesives; as a catalyst in desulfurization of gasoline; use as a reagent for determination of phosphorus and lead	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If soluble molybdenum compounds or liquids containing soluble molybdenum compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If soluble molybdenum compounds or liquids containing soluble molybdenum compounds get on the skin, flush the contaminated skin with water. If soluble molybdenum compounds or liquids containing soluble molybdenum compounds penetrate through the clothing, remove the clothing and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble molybdenum compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble molybdenum compounds or liquids containing soluble molybdenum compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble molybdenum compounds or liquids containing soluble molybdenum compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquids containing soluble molybdenum compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble molybdenum compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOLUBLE MOLYBDENUM COMPOUNDS (AS MOLYBDENUM)

Condition	**Minimum Respiratory Protection* Required Above 5 mg/m^3**
Particulate Concentration	
25 mg/m^3 or less	Any dust or mist respirator**.
50 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter mask respirators**. Any high efficiency particulate filter respirator**.
250 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece** Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
10,000 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**In those cases where eye irritation occurs, full facepiece respirators are recommended. Examples of molybdenum compounds which cause eye irritation are: compounds containing nitrate, acetate, chloride, trioxide, and molybdate.

Occupational Health Guideline for Monomethyl Aniline

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5NH(CH_3)$
- Synonyms: N-Methyl aniline; MA; methyl aniline
- Appearance and odor: Yellow to light brown liquid with a weak, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for monomethyl aniline is 2 parts of monomethyl aniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9 milligrams of monomethyl aniline per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for monomethyl aniline a Threshold Limit Value of 0.5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Monomethyl aniline can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Monomethyl aniline may cause a bluish discoloration of the skin. Headache, dizziness, weakness, drowsiness, and unconsciousness may also occur.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to monomethyl aniline.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to monomethyl aniline at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, liver, kidneys, and blood should be stressed.

—A complete blood count: Monomethyl aniline has been shown to cause methemoglobinemia and anemia in animals. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit and a methemoglobin determination.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Monomethyl aniline vapor causes anoxia due to the formation of methemoglobin. Animal fatalities occurred from daily exposures to 7.6 ppm; signs of intoxication included prostration, labored breathing, and cyanosis; methemoglobinemia developed promptly in rabbits and cats; the rabbits also exhibited mild anemia and bone marrow hyperplasia. Autopsy of animals that died revealed pulmonary involvement ranging from edema to interstitial pneumonia, as well as occasional centrilobular hepatic necrosis and moderate kidney damage. The liquid readily caused poisoning in animals by absorption through the skin. No effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 107.2

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Boiling point (760 mm Hg): 195.6 C (384 F)
3. Specific gravity (water = 1): 0.99
4. Vapor density (air = 1 at boiling point of monomethyl aniline): 3.70
5. Melting point: −80 C (-112 F) (approximately)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Moderate
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid monomethyl aniline with strong acids will cause violent spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving monomethyl aniline.
4. Special precautions: Liquid monomethyl aniline will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 79.4 C (175 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

1. Odor Threshold: Cyanamid's *Chemical Safety Data Sheet* states that monomethyl aniline has a "moderate aniline-type odor," but no quantitative information is available concerning the odor threshold.
2. Eye Irritation Level: Monomethyl aniline vapor is not a known eye irritant.
3. Evaluation of Warning Properties: Since no information is available relating warning properties of monomethyl aniline to air concentrations, the substance is considered to have poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of monomethyl aniline in a bubbler filled with sulfuric acid, followed by treatment with sodium hydroxide, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure monomethyl aniline may be used. An analytical method for monomethyl aniline is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respir tory protection program should be instituted whic includes regular training, maintenance, inspectio cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required use impervious clothing, gloves, face shields (eight-in minimum), and other appropriate protective clothi necessary to prevent skin contact with liquid mo methyl aniline, where skin contact may occur.
- Clothing contaminated with monomethyl anil should be placed in closed containers for storage unt can be discarded or until provision is made for removal of monomethyl aniline from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the monomethyl aniline, the person performing the operation should be informed of monomethyl aniline's hazardous properties.
- Non-impervious clothing which becomes contaminated with monomethyl aniline should be removed immediately and not reworn until the monomethyl aniline is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid monomethyl aniline may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid monomethyl aniline should be immediately washed or showered with soap or mild detergent and water to remove any monomethyl aniline.
- Eating and smoking should not be permitted in areas where liquid monomethyl aniline is handled, processed, or stored.

- Employees who handle liquid monomethyl aniline should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to monomethyl aniline may occur and control methods which may be effective in each case:

Operation	Controls
Use during organic synthesis and in dye intermediates	Process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If monomethyl aniline gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If monomethyl aniline gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If monomethyl aniline soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention.

- **Breathing**

If a person breathes in large amounts of monomethyl aniline, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When monomethyl aniline has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If monomethyl aniline is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Monomethyl aniline may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Monomethyl Aniline," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Cyanamid Corporation: *Chemical Safety Data Sheet – Monomethyl Aniline.*
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RESPIRATORY PROTECTION FOR MONOMETHYL ANILINE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Vapor Concentration	
20 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against monomethyl aniline. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Morpholine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_4H_9ON
- Synonyms: Tetrahydro-1,4-oxazine; diethyleneimide oxide
- Appearance and odor: Colorless liquid with a weak, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for morpholine is 20 parts of morpholine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 70 milligrams of morpholine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Morpholine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Morpholine may cause irritation of the eyes, nose, throat, lungs, and skin.

2. Long-term Exposure: Repeated or prolonged overexposure to morpholine may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to morpholine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to morpholine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from morpholine exposure.

—Chronic respiratory disease: Morpholine causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of morpholine might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Morpholine causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Morpholine causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Eye disease: Morpholine is an eye irritant and has caused corneal edema in workers. Persons with preexisting eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Morpholine is a primary skin irritant and induces hypersensitive responses. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Morpholine vapor is an irritant to the skin, eyes, mucous membranes, and the respiratory tract. Hypersensitivity is common. Repeated daily exposure of rats to 18,000 ppm was lethal to some animals; those dying during the third to fifth days of exposure revealed damage to lungs, liver, and kidneys. A human exposure

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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to 12,000 ppm for 1-½ minutes in a laboratory produced nose irritation and cough; mouth pipetting of the liquid caused a severe sore throat and reddened mucous membranes. The liquid dropped in the eye of a rabbit caused moderate injury with ulceration of the conjunctiva and corneal clouding. Workers exposed for several hours to low vapor concentrations complained of foggy vision with rings around lights, the result of corneal edema which cleared within 3 to 4 hours after cessation of exposure. The liquid is a severe skin irritant and may produce contact dermatitis. In industry, some instances of skin and respiratory tract irritation have been observed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 87.1
2. Boiling point (760 mm Hg): 128 C (263 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of morpholine): 3.0
5. Melting point: −4.8 C (23 F)
6. Vapor pressure at 20 C (68 F): 7 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid morpholine with strong acids will cause violent spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving morpholine.
4. Special precautions: Liquid morpholine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 35 C (95 F) (closed cup)
2. Autoignition temperature: 310 C (590 F)
3. Flammable limits in air, % by volume: Lower: 1.8 (calculated); Upper: 11 (estimated)
4. Extinguishant: Carbon dioxide, dry chemical, alcohol foam

- **Warning properties**

1. Odor Threshold: Grant states that morpholine has a characteristic amine odor. No quantitative information is available concerning the odor threshold, however.

2. Eye Irritation Level: Grant reports that lacrimation has been observed among experimental animals and among industrial workers who have been exposed to high vapor concentrations. "At low concentrations in air, morpholine has been listed with its N-ethyl and N-methyl derivatives among the amines which have been observed to cause transient edema of the cornea and temporary foggy vision with haloes around lights in workers exposed to the vapors for many hours, the symptoms usually coming on after work and clearing spontaneously by the next day."

Patty also reports that morpholine irritates the mucous membranes.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Other Information: Both Patty and Grant note that morpholine is a respiratory tract irritant, but no quantitative information is available concerning the threshold of this irritation.

4. Evaluation of Warning Properties: Since no quantitative information relating warning properties to air concentrations is available, morpholine is treated as a substance with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of morpholine in an adsorption tube containing silica gel, followed by desorption with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure morpholine may be used. An analytical method for morpholine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid morpholine or solutions containing greater than 25% morpholine by weight and to prevent repeated or prolonged skin contact with solutions containing 25% or less of morpholine by weight.
- Clothing contaminated with morpholine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of morpholine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the morpholine, the person performing the operation should be informed of morpholine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid morpholine or solutions containing greater than 25% morpholine by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with liquid morpholine should be removed immediately and not reworn until the morpholine is removed from the clothing.
- Non-impervious clothing which becomes contaminated with morpholine should be removed promptly and not reworn until the morpholine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid morpholine or solutions containing morpholine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid morpholine or solutions containing greater than 15% morpholine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with morpholine should be promptly washed or showered to remove any morpholine.
- Employees who handle liquid morpholine or solutions containing morpholine should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to morpholine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of rubber chemicals for rubber accelerators, catalysts, plasticizers, curing agents, stabilizers of halogenated butyl rubber, and emulsifying agents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a corrosion inhibitor in steam boiler systems, petroleum refining, sterilization autoclaves, and in natural gas processing; use in manufacture of optical brightening agents in bleaches and detergents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in compounding of waxes and polishes for commercial use as automobile waxes, rubless waxes and polishes, and water-resistant polishes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate for textile industry as lubricants, sizing emulsifiers, and softening agents; in pharmaceutical industry as bactericides, analgesics, anesthetics, anti-spasmotics, and anti-malarials; in chemical industry for alkyl morpholines, emulsifying agents, surface-active agents, cosmetics, and soap emulsifiers; in agriculture for protective coatings for fresh fruits and vegetables, pesticide emulsifiers, insecticides, fumigants, and herbicides	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for dyes, waxes, resins, and casein	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid morpholine or solutions containing morpholine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid morpholine or solutions containing morpholine get on the skin, immediately flush the contaminated skin with water. If liquid morpholine or solutions containing morpholine soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of morpholine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When morpholine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If morpholine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Morpholine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Morpholine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on morpholine, look up morpholine in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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- Smyth, H. F., et al.: "Range-Finding Toxicity Data, List V," *Archives of Industrial Hygiene and Occupational Medicine*, 10:61, July 1954.
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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Morpholine*, New York, 1967.

RESPIRATORY PROTECTION FOR MORPHOLINE

Condition	**Minimum Respiratory Protection*** **Required Above 20 ppm**
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Naphtha (Coal Tar)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_7H_8 — C_8H_{10} (approximately)
- Synonyms: Naphtha, 49 degrees Be-coal tar type; crude solvent coal tar naphtha; high-solvent coal tar naphtha
- Appearance and odor: Reddish-brown, mobile liquid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for coal tar naphtha is 100 parts of coal tar naphtha per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 400 milligrams of coal tar naphtha per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Coal tar naphtha can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to coal tar naphtha can cause lightheadedness, drowsiness, and unconsciousness. It also may cause mild irritation of the eyes, nose, and skin.

2. Long-term Exposure: Prolonged overexposure to coal tar naphtha may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to coal tar naphtha.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to coal tar naphtha at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from coal tar naphtha exposure.

—Skin disease: Coal tar naphtha is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although coal tar naphtha is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although coal tar naphtha is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of coal tar naphtha might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Coal tar naphtha vapor is narcotic. Rats survived continuous exposure at 3200 ppm for two months; at 1800 ppm some animals showed damage to the liver and kidneys; above 1000 ppm there was evidence of narcotic action. Rats exposed at 567 ppm and 312 ppm for 18 to 20 hours a day for 7 days had some reduction in blood leukocytes, possibly the result of the presence of benzene. There are few if any well documented reports of industrial injury resulting from the inhalation of

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naphtha. However, exposure to high concentrations might be expected to cause lightheadedness, drowsiness, and possibly irritation of the eyes, nose, and throat. Repeated or prolonged contact with the liquid may result in drying and cracking skin due to defatting action. Coal tar (naphtha) is a non-uniform mixture of aromatic hydrocarbons and may contain benzene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110 (approximately)
2. Boiling point (760 mm Hg): 110 to 190 C (230 to 374 F)
3. Specific gravity (water = 1): 0.97
4. Vapor density (air = 1 at boiling point of coal tar naphtha): 3 (approximately)
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Less than 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving coal tar naphtha.
4. Special precautions: Coal tar naphtha will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 38 to 43 C (100 to 109 F) (closed cup)
2. Autoignition temperature: 482 to 510 C (900 to 950 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Since the odor thresholds of the main constituents of coal tar naphtha are below their permissible exposure limits, the odor threshold of coal tar naphtha is assumed to be below the permissible exposure limit.
2. Eye Irritation Level: According to Grant, Gafafer states that the naphthas cause conjunctival irritation. Two of the main constituents of coal tar naphtha, xylene and toluene, cause noticeable eye irritation at concentrations of 200 and 300 ppm, respectively.
3. Evaluation of Warning Properties: Since the odor threshold of the main constituents of coal tar naphtha are well below their permissible exposure limits, coal tar naphtha is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of coal tar naphtha vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure coal tar naphtha may be used. An analytical method for coal tar naphtha is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).
026).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid coal tar naphtha.
- Clothing wet with liquid coal tar naphtha should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

coal tar naphtha from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the coal tar naphtha, the person performing the operation should be informed of coal tar naphtha's hazardous properties.

- Non-impervious clothing which becomes wet with liquid coal tar naphtha should be removed promptly and not reworn until the coal tar naphtha is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid coal tar naphtha may contact the eyes.

SANITATION

- Skin that becomes wet with liquid coal tar naphtha should be promptly washed or showered with soap or mild detergent and water to remove any coal tar naphtha.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to coal tar naphtha may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of coal-tar paints	Process enclosure; general dilution ventilation; personal protective equipment
Use in preparation of coumarone and indene	General dilution ventilation; personal protective equipment
Use as a solvent in rubber industry in manufacture of waterproof cloth, shoe adhesives, and rubber tires	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent, diluent, or thinner in paint, varnish, and lacquer industries	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in formulations of nitrocellulose and ethylcellulose	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for polymerized styrol, short-oil phenolic varnishes, urea, resins, melamine, and other synthetic resins; use as a solvent for pesticides as DDT and Gammexane	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If coal tar naphtha gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If coal tar naphtha gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If coal tar naphtha soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of coal tar naphtha, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If coal tar naphtha has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If coal tar naphtha is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely

clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Coal tar naphtha should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Coal tar naphtha may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Naphtha (Coal Tar)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR NAPHTHA (COAL TAR)

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Naphthalene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_8$
- Synonyms: White tar; naphthalin
- Appearance and odor: Colorless to brown solid with the odor of mothballs.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for naphthalene is 10 parts of naphthalene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 50 milligrams of naphthalene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Naphthalene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation or ingestion of naphthalene may cause abdominal cramps, nausea, vomiting, diarrhea, headache, tiredness, confusion, painful urination, and bloody or dark urine. Swallowing large amounts may cause convulsions or coma. Inhalation, ingestion, and possibly skin absorption of naphthalene may cause destruction of red blood cells with anemia, fever, yellow jaundice, bloody urine, kidney and liver damage. Naphthalene, on contact with the eyes, has produced irritation. Naphthalene, on contact with the skin, has produced skin irritation.

2. Long-term Exposure: Repeated skin exposure to naphthalene may cause an allergic rash. Repeated exposure may cause cataracts.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to naphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to naphthalene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a deficiency of glucose-6-phosphate dehydrogenase in erythrocytes may be at increased risk from exposure. Examination of the eyes, blood, liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Naphthalene has been shown to cause red blood cell hemolysis. A complete blood count should be performed, including a red cell count, a white cell count, and a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage may also occur from exposure to naphthalene, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Naphthalene vapor causes hemolysis and eye irritation; it may cause cataracts. Severe intoxication from ingestion of the solid results in characteristic manifestations of marked intravascular hemolysis and its consequences, including potentially fatal hyperkalemia. Initial symptoms include eye irritation, headache, confu-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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sion, excitement, malaise, profuse sweating, nausea, vomiting, abdominal pain, and irritation of the bladder; there may be progression to jaundice, hematuria, hemoglobinuria, renal tubular blockage, and acute renal shutdown. Hematologic features include red cell fragmentation, icterus, severe anemia with nucleated red cells, leukocytosis, and dramatic decreases in hemoglobin, hematocrit, and red cell count; sometimes there is formation of Heinz bodies and methemoglobin. Individuals with a deficiency of glucose-6-phosphate dehydrogenase in erythrocytes may be more susceptible to hemolysis by naphthalene. Cataracts and ocular irritation have been produced experimentally in animals and have been described in humans; of 21 workers exposed to high concentrations of fume or vapor for 5 years, 8 had peripheral lens opacities; in other studies no abnormalities of the eyes have been detected in workers exposed to naphthalene for several years. The vapor causes eye irritation at 15 ppm; eye contact with the solid may result in conjunctivitis, superficial injury to the cornea, chorioretinitis, scotoma, and diminished visual acuity. Naphthalene on the skin may cause hypersensitivity dermatitis; chronic dermatitis is rare.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 128.2
2. Boiling point (760 mm Hg): 218 C (424 F)
3. Specific gravity (water = 1): 1.14
4. Vapor density (air = 1 at boiling point of naphthalene): 4.4
5. Melting point: 74 – 80 C (165 – 176 F)
6. Vapor pressure at 20 C (68 F): 0.05 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.003
8. Evaporation rate (butyl acetate = 1): Much less than 1

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as dense acrid smoke and carbon monoxide) may be released in a fire involving naphthalene.
4. Special precautions: Melted naphthalene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 79 C (174 F) (closed cup)
2. Autoignition temperature: 526 C (979 F)
3. Flammable limits in air, % by volume: Lower: 0.9; Upper: 5.9
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* reports that the odor threshold of naphthalene is "at least as low as 0.3 ppm."
2. Eye Irritation Level: The *Hygienic Guide* states that "naphthalene vapor is reported to cause eye irritation at 15 ppm or above in air."
3. Evaluation of Warning Properties: Through its odor and irritant effects, naphthalene can be detected at or below the permissible exposure limit. Naphthalene, therefore, is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure naphthalene may be used. An analytical method for naphthalene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with naphthalene or liquids containing naphthalene.
- If employees' clothing may have become contaminated with solid naphthalene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with naphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of naphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the naphthalene, the person performing the operation should be informed of naphthalene's hazardous properties.
- Non-impervious clothing which becomes contaminated with naphthalene should be removed promptly and not reworn until the naphthalene is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid naphthalene or liquids containing naphthalene may contact the eyes.

SANITATION

- Skin that becomes contaminated with naphthalene should be promptly washed or showered with soap or mild detergent and water to remove any naphthalene.
- Eating and smoking should not be permitted in areas where solid naphthalene is handled, processed, or stored.
- Employees who handle naphthalene or liquids containing naphthalene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to naphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of insecticide and moth repellant as flakes, powder, balls, or cakes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a fumigant for moth repellant and insecticide	General dilution ventilation; personal protective equipment
Use in manufacture of chemical intermediates for production of pharmaceuticals, resins, dyes, plasticizers, solvents, coatings, insecticides, pigments, rubber chemicals, tanning agents, surfactants, waxes, cable coatings, textile spinning lubricants, rodenticides, and in storage batteries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of naphthalene	Local exhaust ventilation; process enclosure; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If naphthalene or liquids containing naphthalene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If molten naphthalene gets on the skin, immediately flush the skin with large amounts of water. Get medical attention immediately. If naphthalene or liquids containing naphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If naphthalene or liquids containing naphthalene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of naphthalene, move the exposed person to fresh air at once.

- **Swallowing**

When naphthalene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify some-

one else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If naphthalene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.

- Waste disposal methods:

Naphthalene may be disposed of:

1. By making packages of naphthalene in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving naphthalene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on naphthalene, look up naphthalene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Naphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR NAPHTHALENE

Condition	**Minimum Respiratory Protection*** **Required Above 10 ppm**
Particulate and Vapor Concentration	
500 ppm or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust filter. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

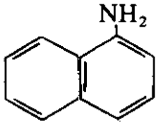
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
alpha-NAPHTHYLAMINE
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about alpha-naphthylamine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{10}H_9N$
- **Structure:**



- **Synonyms:** 1-Naphthylamine; 1-aminonaphthalene; naphthalidam; naphthalidine
- **Identifiers:** CAS 134-32-7; RTECS QM1400000; DOT 2077, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless to yellow crystals which darken in air to a reddish purple color with a weak ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 143.20
2. Boiling point (at 760 mmHg): 301°C (573.8°F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of alpha-naphthylamine): 4.93
5. Melting point: 50°C (122°F)
6. Vapor pressure at 104°C (219°F): 1 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 0.17

- **Reactivity**

1. Incompatibilities: alpha-naphthylamine oxidizes in air
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving alpha-naphthylamine.

- **Flammability**

1. Flash point: 157°C (315°F) (closed cup)
2. Extinguishant: Water, dry chemical, carbon dioxide, or alcohol foam
3. Combustible solid, Flammability Rating 1 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for alpha-naphthylamine; however, the OSHA standard requires implementation of stringent controls wherever alpha-naphthylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of alpha-naphthylamine are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedure"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1004, alpha-Naphthylamine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have an assigned threshold limit value (TLV®) for alpha-naphthylamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

alpha-Naphthylamine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* In mice and dogs, chronic oral administration or subcutaneous injection of alpha-naphthylamine produced inconclusive evidence of liver, bladder, lung, or lymphatic cancer; however, beta-naphthylamine, which is a contaminant in commercial grade alpha-naphthylamine, is a recognized animal carcinogen. In addition, certain metabolites of alpha-naphthylamine have been shown to be carcinogenic in animals (e.g., N-(1-naphthyl)-hydroxylamine induces bladder cancer in mice, and 1-nitrosonaphthalene induces tumors in rats).

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2. *Effects on humans:* Long-term exposure of workers to commercial alpha-naphthylamine (which contains 4%-10% beta-naphthylamine) has been associated with an increased incidence of bladder cancer.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to alpha-naphthylamine can cause mild skin and eye irritation.
2. *Long-term (chronic):* Exposure to alpha-naphthylamine can cause headache, dizziness, a feeling of euphoria, weakness, impaired muscular coordination (ataxia), bluish discoloration of skin and mucous membranes (due to methemoglobinemia), breathing difficulty (dyspnea), blood in the urine, and painful, difficult, or frequent urination.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to alpha-naphthylamine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, lymphatic system, and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to alpha-naphthylamine. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to alpha-naphthylamine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, lymphatic system, and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to alpha-naphthylamine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting alpha-naphthylamine dust with glass-fiber filters and silica gel tubes followed by elution with acetic acid in 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure alpha-naphthylamine may also be used if available. A detailed sampling and analytical method for alpha-naphthylamine may be found in the *NIOSH Manual of Analytical Methods* (method number 264).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where alpha-naphthylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body

CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where alpha-naphthylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with alpha-naphthylamine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of alpha-naphthylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of alpha-naphthylamine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove alpha-naphthylamine from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1004:

Areas where alpha-naphthylamine is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of alpha-naphthylamine, local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving alpha-naphthylamine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of alpha-naphthylamine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where alpha-naphthylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of alpha-naphthylamine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove alpha-naphthylamine from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to alpha-naphthylamine may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for alpha-naphthylamine

Operations	Controls
During use in the manufacture of dyes, herbicides, and rubber antioxidants; during use in research facilities and laboratories	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker comes in contact with alpha-naphthylamine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to alpha-naphthylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If alpha-naphthylamine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to alpha-naphthylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If alpha-naphthylamine gets on the skin, wash it immediately with soap and water. If alpha-naphthylamine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and supplied-air respirators) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If alpha-naphthylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, alpha-naphthylamine may be collected and placed in an appropriate container.
4. alpha-Naphthylamine solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of alpha-naphthylamine are prohibited by OSHA. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.
5. For small quantities of liquids containing alpha-naphthylamine, absorb on paper towels and place in an appropriate container.
6. Large quantities of liquids containing alpha-naphthylamine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for alpha-naphthylamine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

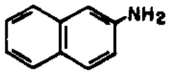
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR beta-NAPHTHYLAMINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about beta-naphthylamine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{10}H_9N$
- **Structure:**



- **Synonyms:** 2-Naphthylamine, 2-aminonaphthalene, 2-naphthalamine, 2-naphthalenamine
- **Identifiers:** CAS 91-59-8; RTECS QM2100000; DOT 1650, label required: "Poison"
- **Appearance and odor:** Odorless, white to reddish, crystals which darken in air to a reddish-purple color

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 143.20
2. Boiling point (at 760 mmHg): 306 °C (583 °F)
3. Specific gravity (water = 1): 1.061
4. Vapor density (air = 1 at boiling point of beta-naphthylamine): 4.95
5. Melting point: 110.2 °C (230.4 °F)
6. Vapor pressure at 108 °C (226.4 °F): 1 mmHg
7. Soluble in water

- **Reactivity**

1. Incompatibilities: beta-Naphthylamine oxidizes slowly in the presence of air and light.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving beta-naphthylamine.

- **Flammability**

1. Extinguishant: Dry chemical, foam, carbon dioxide, water
2. Combustible solid, no NFPA flammability rating

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for beta-naphthylamine; however, the OSHA standard requires implementation of stringent controls wherever beta-naphthylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of beta-naphthylamine are manufactured, processed, repackaged, packaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1009, beta-Naphthylamine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated beta-naphthylamine as an A1 substance (confirmed human carcinogen). The ACGIH recommends that no exposure or contact by any route be permitted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

beta-Naphthylamine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Chronic oral administration of beta-naphthylamine produced liver cancer in mice and bladder cancer in hamsters, dogs, and monkeys.
2. *Effects on humans:* Acute exposure to beta-naphthylamine dust or vapor has caused bladder inflammation with bleeding (hemorrhagic cystitis). Chronic exposure to beta-naphthylamine alone or to beta-naphthylamine as an impurity in other compounds has been associated with an increased incidence of bladder cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to beta-naphthylamine can cause weakness, dizziness, feeling of euphoria, breathing difficulty (dyspnea), bluish discoloration of the skin and mucous membranes (due to methemoglobinemia), and irritation of the skin and eyes.
2. *Long-term (chronic):* Exposure to beta-naphthylamine can cause frequent, painful, or difficult urination or blood in the urine.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

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- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to beta-naphthylamine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

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1. Acute SHE's include: Contact and/or allergic dermatitis.
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Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where beta-naphthylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting from a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where beta-naphthylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with beta-naphthylamine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of beta-naphthylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beta-naphthylamine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

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Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

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Containers of beta-naphthylamine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove beta-naphthylamine from materials, equipment, and the decontamination facility.

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Table 1.—Operations and methods of control for beta-naphthylamine

Operations	Controls
During use in the manufacture of dyes, acids, and rubber; during use in research facilities and laboratories	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker comes in contact with beta-naphthylamine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to beta-naphthylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If beta-naphthylamine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to beta-naphthylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If beta-naphthylamine gets on the skin, wash it immediately with soap and water. If beta-naphthylamine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If beta-naphthylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, beta-naphthylamine may be collected and placed in an appropriate container.
4. beta-Naphthylamine solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it should then be placed in an appropriate container. Dry sweeping and dry mopping of beta-naphthylamine are prohibited by OSHA. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.
5. For small quantities of liquids containing beta-naphthylamine, absorb on paper towels and place in an appropriate container.
6. Large quantities of liquids containing beta-naphthylamine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for beta-naphthylamine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Nickel Carbonyl*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Ni(CO)_4$
- Synonyms: None
- Appearance and odor: Colorless liquid with a musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nickel carbonyl is 0.001 part of nickel carbonyl per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.007 milligram of nickel carbonyl per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be retained, but has recommended that nickel carbonyl be regulated as an occupational carcinogen. The NIOSH Special Occupational Hazard Review for Nickel Carbonyl and the NIOSH Criteria Document for Inorganic Nickel should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nickel carbonyl can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Depending on the severity of inhalation exposure, both initial and delayed symptoms may develop. Initial symptoms include dizziness, headache, shortness of breath, and vomiting. These symptoms generally disappear when the individual is removed from exposure. The delayed symptoms may develop 12 to 36 hours after exposure. These symptoms include chest pain, cough, rapid breathing, shortness of breath, a bluish discoloration of the skin, and increased temperature. Delirium and other signs of nervous system problems usually appear at this time. In some cases the two stages may merge. In severe cases death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to nickel carbonyl has been associated with an increased incidence of cancer of the lungs and sinuses.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nickel carbonyl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel carbonyl at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs and upper respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Nickel carbonyl causes human lung damage and is a suspected lung carcinogen. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nickel carbonyl is a severe pulmonary irritant. Persons with decreased pulmonary function may be at increased risk from exposure.

—Sputum cytology: Nickel carbonyl is associated with an increase of lung cancer in humans.

—Urinalysis: Since kidney damage has been observed from exposure, a urinalysis should be performed to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Examination of the urine for nickel should be conducted on a monthly basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, with the exception that a urinalysis should be conducted on a monthly basis.

- **Summary of toxicology**

Nickel carbonyl vapor is a severe pulmonary irritant and probably causes cancer of the paranasal sinuses and the lungs in animals and man. Initial symptoms of overexposure usually include frontal headache, vertigo, nausea, vomiting, and sometimes substernal and epigastric pain; generally these early effects disappear when the individual is removed to fresh air. There may be an asymptomatic interval between recovery from initial symptoms and the onset of delayed symptoms, which tend to develop 12 hours or more following exposure; constrictive pain in the chest is characteristic of the delayed onset of pulmonary effects, followed by cough, hyperpnea and cyanosis, leading to profound weakness; gastrointestinal symptoms may also occur. The temperature seldom rises above 101 F, and leukocytosis above 12,000 per mg/m^3 is infrequent. Physical signs compatible with pneumonitis or bronchopneumonia are elicited in the chest. Except for the pronounced weakness and hyperpnea, the physical findings and symptoms resemble those of a viral or influenzal pneumonia. Terminally, delirium and convulsions frequently occur; death has occurred from 3 to 13 days after exposure to nickel carbonyl. In subjects who recover from nickel carbonyl intoxication, convalescence is usually protracted (2 to 3 months) and is characterized by excessive fatigue on slight exertion. Exposure of rats to nickel carbonyl has caused pulmonary carcinomata; multiple intravenous injection of nickel carbonyl in rats has caused carcinomata and sarcomata in diverse organs, including the liver and kidneys. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on nickel carbonyl vapor, although there are usually concurrent exposures to respirable particles of nickel, nickel subsulfide, and nickel oxide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 170.7
2. Boiling point (760 mm Hg): 43 C (109 F)
3. Specific gravity (water = 1): 1.32
4. Vapor density (air = 1 at boiling point of nickel carbonyl): 5.89
5. Melting point: −25 C (−13 F)
6. Vapor pressure at 20 C (68 F): 321 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.018
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Liquid nickel carbonyl may explode when heated above 60 C (140 F). In the presence of air, nickel carbonyl forms a deposit which becomes peroxidized. This tends to decompose and ignite.
2. Incompatibilities: Contact with nitric acid, chlorine, and other oxidizers may cause fires and explosions. The vapor of nickel carbonyl may promote the ignition of mixtures of combustible vapors (such as gasoline) and air.
3. Hazardous decomposition products: Toxic gases and vapors (such as nickel oxide fume and carbon monoxide) may be released in a fire involving nickel carbonyl.
4. Special precautions: Liquid nickel carbonyl will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Lower than −20 C (−4 F) (closed cup)
2. Autoignition temperature: May ignite spontaneously
3. Flammable limits in air, % by volume: Lower: 2; Upper: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Patty states that the odor of nickel carbonyl is detectable at between 1 and 3 ppm.
2. Eye Irritation Level: According to the AIHA *Hygienic Guide*, the effect of eye contact with nickel carbonyl is unknown. This substance is not known to be an eye irritant, however.
3. Evaluation of Warning Properties: Since the odor threshold of nickel carbonyl is over 1000 times greater than the permissible exposure limit, nickel carbonyl is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Measurement of nickel carbonyl may be done by sampling with a bubbler containing alcoholic-iodine solution, followed by chemical treatment and colorimetric analysis. The NIOSH Special Occupational Hazard Review for Nickel Carbonyl suggests a detailed method which may be employed for sampling and analyzing nickel carbonyl.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nickel carbonyl.
- Any clothing which becomes wet with liquid nickel carbonyl should be removed immediately and not reworn until the nickel carbonyl is removed from the clothing.
- Clothing wet with liquid nickel carbonyl should be placed in vapor-tight, sealed containers for storage until it can be discarded or until provision is made for the removal of nickel carbonyl from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nickel carbonyl, the person performing the operation should be informed of nickel carbonyl's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nickel carbonyl contacting the eyes.

SANITATION

- Skin that becomes wet with liquid nickel carbonyl should be immediately washed or showered to remove any nickel carbonyl.
- Eating and smoking should not be permitted in areas where nickel carbonyl is handled, processed, or stored.
- Employees who handle nickel carbonyl should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nickel carbonyl may occur and control methods which may be effective in each case:

Operation	Controls
Use in Mond process for nickel refining	Process enclosure; local exhaust ventilation; personal protective equipment
Use in plating operations on foundry patterns, steel, and electronics manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a reagent in synthesis of acrylic esters; use as a catalyst or reagent in organic synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Use in petroleum and petrochemical processing (including methanation of ammonia synthesis gas)	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid nickel carbonyl gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid nickel carbonyl gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid nickel carbonyl soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of nickel carbonyl, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid nickel carbonyl has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nickel carbonyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Nickel carbonyl should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Nickel carbonyl may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

Nickel carbonyl appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 11, 1976.

RESPIRATORY PROTECTION FOR NICKEL CARBONYL

Condition	**Minimum Respiratory Protection* Required Above 0.001 ppm**
Greater than 0.001 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against nickel carbonyl. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Nickel Metal and Soluble Nickel Compounds

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble nickel compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Nickel, metallic

- Formula: Ni
- Synonyms: Nickel catalyst; Raney nickel
- Appearance and odor: Silvery gray, metallic (or darker), odorless powder.

Nickel nitrate hexahydrate

- Formula: $Ni(NO_3)_2{-}_6H_2O$
- Synonyms: None
- Appearance and odor: Green, odorless solid.

Nickel sulfate hexahydrate

- Formula: $NiSO_4{-}_6H_2O$
- Synonyms: None
- Appearance and odor: Green, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nickel metal and soluble nickel compounds is 1 milligram of nickel metal and soluble nickel compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for nickel be reduced to 0.015 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, and that nickel be regulated as an occupational carcinogen. The NIOSH Criteria Document for Inorganic Nickel and the Special Occupational Hazard Review for Nickel Carbonyl should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Metallic nickel or soluble nickel compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Nickel fumes are respiratory irritants and may cause pneumonitis. Skin contact may cause an allergic skin rash. Nickel and its compounds have been reported to cause cancer of the lungs and sinuses. Nickel itself is not very toxic if swallowed, but its soluble salts are quite toxic and, if swallowed, may cause giddiness and nausea. Exposure to nickel carbonyl (by inhalation or skin absorption) may cause both initial and delayed symptoms. Initial symptoms include headache, dizziness, shortness of breath, and vomiting. These symptoms generally disappear when the worker is exposed to fresh air. The delayed symptoms may develop 12 to 36 hours after exposure. The shortness of breath returns, a blue color of the skin may appear, and a fever may develop. The exposed person may become delirious. In some cases the symptoms may run together. Death may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nickel metal and soluble nickel compounds.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel metal and soluble nickel compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to nickel metal and soluble nickel compounds would be expected to be at increased risk from exposure. Examination of the nasal cavities and lungs should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Nickel metal and soluble nickel compounds cause human lung damage and cancer of the lung. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nickel metal and soluble nickel compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Nickel metal and soluble compounds are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Metallic nickel and certain soluble nickel compounds as dust or fume cause sensitization dermatitis and probably produce cancer of the paranasal sinuses and the lung; nickel fume in high concentrations is a respiratory irritant. Severe but transient pneumonitis in two workers resulted from exposure to nickel fume; in one case, exposure was for 6 hours, and post-incident sampling suggested a nickel concentration of 0.26 mg/m^3. "Nickel itch" is a dermatitis resulting from sensitization to nickel; the first symptom is usually itching, which occurs up to 7 days before skin eruption appears. The primary skin eruption is erythematous, or follicular; it may be followed by superficial discrete ulcers, which discharge and become crusted, or by eczema; in the chronic stages, pigmented or depigmented plaques may be formed. Nickel sensitivity, once acquired, is apparently not lost; recovery from the dermatitis usually occurs within 7 days of cessation of exposure, but may take several weeks. A worker who had developed cutaneous sensitization also developed apparent asthma from inhalation of nickel sulfate; immunologic studies showed circulating antibodies to the salt, and controlled exposure to a solution of nickel sulfate resulted in decreased pulmonary function and progressive dyspnea; the possibility of developing hypersensitivity pneumonitis could not be excluded. In animals, finely divided metallic nickel was carcinogenic when introduced into the pleural cavity, muscle tissue, and subcutaneous tissues; rats and guinea pigs exposed to a concentration of 15 mg/m^3 of powdered metallic nickel developed malignant pulmonary neoplasms. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on respirable particles of nickel, nickel subsulfide, nickel oxide, and on nickel carbonyl vapor. Many of the studies also included exposures to other suspected carcinogens.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Nickel, metallic**

1. Molecular weight: 58.7
2. Boiling point (760 mm Hg): 2730 C (4946 F)
3. Specific gravity (water = 1): 8.9
4. Vapor density (air = 1 at boiling point of metallic nickel): Not applicable
5. Melting point: 1453 C (2648 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Nickel nitrate hexahydrate**

1. Molecular weight: 290.8
2. Boiling point (760 mm Hg): 137 C (278 F) (loses water)
3. Specific gravity (water = 1): 2.05
4. Vapor density (air = 1 at boiling point of nickel nitrate hexahydrate): Not applicable
5. Melting point: 57 C (135 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 60
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Nickel sulfate hexahydrate**

1. Molecular weight: 262.8
2. Boiling point (760 mm Hg): 103 C (217 F) (loses water)
3. Specific gravity (water = 1): 2.07
4. Vapor density (air = 1 at boiling point of nickel sulfate hexahydrate): Not applicable
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 40
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat (nickel only)
2. Incompatibilities: Contact of nickel with strong acids may form flammable and explosive hydrogen gas.

Contact with sulfur may cause evolution of heat. Contact of nickel nitrate with wood and other combustibles may cause fire.

3. Hazardous decomposition products: Toxic gases and vapors (such as nickel carbonyl and oxides of nitrogen) may be released in a fire involving nickel or in the decompostion of nickel compounds.

4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: Not available
3. Minimum explosive concentration: Not available, but nickel sponge catalyst may ignite spontaneously in air.
4. Extinguishant: Dry powder, dry sand, dry dolomite, dry graphite

- **Warning properties**

Grant states that "workers employed in nickel plating involving nickel sulfate, sulfuric acid, and chlorine are said to have developed conjunctivitis and epiphora when ventilation was poor." Since, according to Grant, "both sulfuric acid mist and chlorine gas are known to cause burning and stinging of the eyes," and since the AIHA *Hygienic Guide* states that eye contact "does not present any problem peculiar to nickel," nickel metal and soluble compounds are not treated as eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by treatment with nitric and perchloric acids, solution in nitric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for nickel metal and soluble nickel compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).
number PB 258 433).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with powdered metallic nickel or solids or liquids containing soluble nickel compounds.
- If employees' clothing may have become contaminated with powdered metallic nickel or solid soluble nickel compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with metallic nickel or soluble nickel compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of metallic nickel or soluble nickel compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the metallic nickel or soluble nickel compounds, the person performing the operation should be informed of these substances's hazardous properties.
- Non-impervious clothing which becomes contaminated with metallic nickel or soluble nickel compounds should be removed promptly and not reworn until the metallic nickel or soluble nickel compounds are removed from the clothing.

SANITATION

- Skin that becomes contaminated with metallic nickel or soluble nickel compounds should be promptly washed or showered with soap or mild detergent and water to remove any metallic nickel or soluble nickel compounds.
- Eating and smoking should not be permitted in areas where solids or liquids containing soluble nickel compounds are handled, processed, or stored.
- Employees who handle powdered metallic nickel or solids or liquids containing soluble nickel compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to nickel metal and soluble nickel compounds may occur should be identified by

signs or appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nickel metal and soluble nickel compounds may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture and fabricating of more than 3000 alloys; use in electronic tube parts, coins heavy machinery, tools, instrument parts, magnets, food and chemical processing equipment, flatware, jet engines, automotive parts, zippers, nickel anodes, surgical and dental instruments, and cooking utensils (they aid in corrosion- and heat-resistance, enhance ductibility, and increase thermal conductivity)	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during processing and refining of ore	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of nickel-iron alloys, and non-ferrous-nickel alloys	Local exhaust ventilation; general dilution ventilation
Use during fabrication of nickel-plated materials	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as starting material of complex compounds; use as catalysts in hydrogenation of fats/oils	General dilution ventilation
Use in textile industry in dyeing and printing; and in ceramic industry in coloring	General dilution ventilation; local exhaust ventilation

Operation	Controls
Use of metal and salts during electroplating and electroless plating	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of nickel-iron alloys and non-ferrous-nickel alloys	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Skin Exposure**

If solids or liquids containing soluble nickel compounds get on the skin, immediately flush the contaminated skin with water. If solids of liquids containing soluble nickel compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. Metallic nickel should be removed from the skin by washing with soap or mild detergent and water.

- **Breathing**

If a person breathes in large amounts of metallic nickel of soluble nickel compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible. If any nickel carbonyl has been inhaled, get medical attention promptly.

- **Swallowing**

When metallic nickel or solids or liquids containing soluble nickel compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If nickel metal and soluble nickel compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing nickel should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Nickel metal and soluble nickel compounds may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

Nickel metal and soluble nickel compounds appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 11, 1976.

RESPIRATORY PROTECTION FOR NICKEL METAL AND SOLUBLE COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Dust or Mist Concentration	
5 mg/m³ or less	Any dust and mist respirator.
10 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

RESPIRATORY PROTECTION FOR NICKEL METAL AND SOLUBLE COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Dust, Mist, or Fume Concentration	
10 mg/m³ or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Nicotine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_{14}N_2$
- Synonyms: 3-(1-Methyl-2-pyrrolidyl)pyridine
- Appearance and odor: Pale yellow to dark brown liquid with a slight fishy odor when warm.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nicotine is 0.5 milligram of nicotine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nicotine can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may rapidly enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: The action of nicotine is rapid either after breathing it, swallowing it, or absorbing it through the skin. Exposure to it may cause a burning sensation of the mouth and throat, abdominal pain, nausea, vomiting, and diarrhea. It may also cause headache, sweating, dizziness, hearing and visual disturbances, confusion, weakness, and incoordination. The heart may beat irregularly or stop. Trembling and convulsions, faintness, shortness of breath, and collapse may occur which may be followed by death from respiratory paralysis. Exposure of the eyes and skin may cause irritation. Nicotine has caused abnormalities in the offspring of laboratory animals.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nicotine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nicotine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the nervous system and cardiovascular system should be stressed.

2. Periodic Medical Examination: The aforementioned medical examination should be repeated on an annual basis.

- **Summary of toxicology**

Nicotine in solution causes a transient stimulation, followed by depression or paralysis of the central nervous system, peripheral autonomic ganglia, and nerve endings in skeletal muscle; it also directly stimulates smooth muscle. Many fatal human cases of nicotine intoxication have occurred, usually as a result of accidental or suicidal ingestion of nicotine insecticides. Nicotine is readily absorbed through the skin; in fatal cases of intoxication, death nearly always occurs within 1 hour and has occurred within 1 minute; the fatal adult dose is about 60 mg. Symptoms include nausea, salivation, abdominal pain, vomiting, diarrhea, cold sweat, headache, dizziness, disturbed hearing and vision, confusion, weakness, and incoordination. Initially, respiration is deep and rapid, blood pressure is elevated, and the pulse is slow; intense vagal stimulation may cause transient cardiac standstill or paroxysmal atrial fibrillation; the pupils are generally constricted. Excitation of the central nervous system results in tremor and sometimes clonic-tonic convulsions. As central nervous system

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depression ensues the pupils dilate, the blood pressure falls, and the pulse becomes rapid and often irregular; faintness, prostration, dyspnea, and paralysis of respiratory muscles are followed by death. Recovery usually occurs if the victim survives 1 to 4 hours. Skeletal system malformations occurred in the offspring of pregnant mice injected subcutaneously with nicotine between days 9 to 11 of pregnancy.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 162
2. Boiling point (760 mm Hg): 266 C (511 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of nicotine): 5.6
5. Melting point: −79 C (−110 F)
6. Vapor pressure at 20 C (68 F): 0.0425 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions below 60 C (140 F)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause violent spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nicotine.
4. Special precautions: Nicotine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 95 C (203 F) (calculated)
2. Autoignition temperature: 244 C (471 F)
3. Flammable limits in air, % by volume: Lower: 0.7; Upper: 4.0
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: Grant reports one case where exposure caused "a severe pain, much conjunctival reaction and corneal infiltration. Eventually the eye healed with partial opacification of the cornea."
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of nicotine, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of nicotine on resin with subsequent desorption with ethyl acetate and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nicotine may be used. An analytical method for nicotine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).
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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nicotine.
- Clothing which has had any possibility of being contaminated with liquid nicotine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nicotine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nicotine, the person performing the operation should be informed of nicotine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid nicotine, facilities for quick

drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with liquid nicotine should be removed immediately and not reworn until the nicotine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nicotine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid nicotine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid nicotine should be immediately washed or showered with soap or mild detergent and water to remove any nicotine.
- Eating and smoking should not be permitted in areas where liquid nicotine is handled, processed, or stored.
- Employees who handle liquid nicotine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nicotine may occur and control methods which may be effective in each case:

Operation	Controls
Application as a pesticide and fumigant on vegetable crops, fruit, grasses and turf, and greenhouse plants and crops	Personal protective equipment
Formulation of pesticide products and fumigants	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Liberation as a by-product during tobacco processing and manufacture of tobacco products	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Extraction and handling of nicotine	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid nicotine or solutions of nicotine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid nicotine or solutions of nicotine get on the skin, immediately flush the contaminated skin with water. If liquid nicotine or solutions of nicotine soak through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of nicotine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid nicotine or solutions of nicotine have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nicotine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Nicotine may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR NICOTINE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
35 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 35 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nicotine; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 35 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Nitric Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HNO_3
- Synonyms: Aqua fortis; white fuming nitric acid (WFNA); red fuming nitric acid (RFNA); hydrogen nitrate
- Appearance and odor: Colorless, yellow, or red fuming liquid with a suffocating, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitric acid is 2 parts of nitric acid per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of nitric acid per cubic meter of air (mg/m^3). NIOSH has recommended a permissible exposure limit of 2 ppm averaged over a work shift of up to ten hours per day, forty hours per week. The NIOSH Criteria Document for Nitric Acid should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitric acid can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Nitric acid vapor or mist is an irritant of the eyes, nose, throat, and skin. Liquid nitric acid or high concentrations of nitric acid vapor may cause severe burns of the eyes with permanent damage. Liquid nitric acid or high concentrations of nitric acid vapor may produce skin burns and ulcers. Nitric acid may stain the skin a bright yellow. Exposure to high concentrations of nitric acid vapor may cause severe breathing difficulties which may be delayed in onset and may also cause pneumonia. Swallowing nitric acid may cause burns of the mouth, throat, and stomach.

2. Long-term Exposure: Repeated or prolonged exposure to nitric acid mists or strong concentrations of nitric acid vapors may cause erosion of the exposed teeth.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitric acid at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, skin, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Nitric acid causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nitric acid is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Eye disease: Nitric acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—Skin disease: Weak nitric acid is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or at some other frequency to be determined by the responsible physician.

- **Summary of toxicology**

Nitric acid vapor or mist is an irritant of the eyes, mucous membranes, and skin. When nitric acid is exposed to air or comes in contact with organic matter, it decomposes to yield a mixture of toxic oxides of nitrogen, including nitric oxide and nitrogen dioxide. Exposure to high concentrations of nitric acid vapor or mist causes pneumonitis and pulmonary edema which may be fatal; onset of symptoms may be delayed for 4 to 30 hours. In contact with the eyes, the liquid produces severe burns which may result in permanent damage and visual impairment. On the skin, the liquid or concentrated vapor produces immediate, severe and penetrating burns; concentrated solutions cause deep ulcers and stain the skin a bright yellow or yellowish-brown color. The vapor and mist may erode the exposed teeth. Ingestion of the liquid will cause immediate pain and burns of the mouth, esophagus, and gastrointestinal tract.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 63 (solute)

2. Boiling point (760 mm Hg): 121.6 C (251 F) (for "constant boiling," 68%); 84 C (183 F) (white fuming nitric acid); 60 C (140 F) (red fuming nitric acid)

3. Specific gravity (water = 1): 1.41 (constant boiling); 1.5 (white fuming); 1.55 (red fuming)

4. Vapor density (air = 1 at boiling point of nitric acid): 2 – 3 approximately

5. Melting point: −41 C (−42 F) (for "constant boiling," 68%); −41.6 C (−43 F) (white fuming); −52 C (−61 F) (red fuming)

6. Vapor pressure at 20 C (68 F): 2.9 mm Hg (HNO3) (constant boiling), 2.6 mm Hg (H2O) (constant boiling); 62 mm Hg (white fuming); 103 mm Hg (red fuming)

7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst and liberate toxic oxides of nitrogen.

2. Incompatibilities: Reacts explosively with combustible organic or readily oxidizable materials such as wood, turpentine, metal powders, hydrogen sulfide, etc. Contact with strong bases may cause violent spattering.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitric acid decomposes.

4. Special precautions: Nitric acid will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but is a strong oxidizer.

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of nitric acid.

2. Eye Irritation Level: The AIHA *Hygienic Guide*, concerning eye contact with nitric acid, states that "nitric acid produces very severe immediate damage which may result in permanent damage and visual impairment."

3. Other Information: The AIHA *Hygienic Guide* notes that "'nitrous fumes,' expressed in terms of nitrogen dioxide, may cause immediate irritation of the throat at concentrations as low as 62 ppm."

4. Evaluation of Warning Properties: Patty points out that "nitric acid manufacture is more hazardous than hydrochloric acid manufacture in that . . . the oxides of nitrogen have inadequate warning properties in low, toxic concentrations." For the purposes of this guideline, nitric acid is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Nitric acid may be measured by collection of nitric acid in a midget impinger, followed by ultraviolet spectrophotometric analysis. An analytical method for nitric acid is in the *NIOSH Manual of Analytical Methods*, 2nd

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nitric acid or liquids containing nitric acids having a pH equal to or less than 2.5.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing nitric acid having a pH greater than 2.5.
- Clothing contaminated with nitric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitric acid, the person performing the operation should be informed of nitric acid's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid nitric acid or solutions containing nitric acid having a pH equal to or less than 2.5, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with nitric acid should be removed immediately and not reworn until the nitric acid is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nitric acid or solutions containing nitric acid contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid nitric acid or solutions containing nitric acid having a pH equal to or less than 2.5, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with nitric acid should be immediately washed or showered to remove any nitric acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitric acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in metallurgy as a pickling agent; in metal refining, ore recovery, metal etching, and photoengraving	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in acidulation of phosphate rock and manufacture of nitrogen solutions for use in fertilizer industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a laboratory reagent; in wood pulping industry	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during inorganic synthesis in manufacture of fertilizers, explosives, herbicides, antibiotics, meat-curing, pickling, ceramics, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during organic synthesis in manufacture of nitrating and oxidizing agents, nylons, foams, lubricants, insecticides, dyes, explosives, photographic films, lacquers, and celluloids	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If nitric acid or strong concentrations of nitric acid vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If nitric acid or strong concentrations of nitric acid vapors get on the skin, immediately flush the contaminated skin with water. If nitric acid soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of nitric acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When nitric acid has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the nitric acid. Do not attempt to make the exposed person vomit. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nitric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Flush with copious quantities of water and neutralize with alkaline material (such as soda ash, lime, etc)..

- Waste disposal method:

Nitric acid may be disposed of by neutralizing with water and alkaline material (such as soda ash, lime, etc). and disposing in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR NITRIC ACID

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate or Vapor Concentration	
250 mg/m³ or less	A chemical cartridge respirator with a full facepiece providing protection against nitric acid.** A gas mask with a chin-style or a front- or back-mounted organic vapor canister providing protection against nitric acid. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m³*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against nitric acid. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Nitric acid is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore and should not be used to provide protection against nitric acid. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitric acid; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 250 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Nitric Oxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: NO
- Synonyms: Nitrogen monoxide
- Appearance and odor: Colorless gas with a sharp, sweet odor. In high concentrations, nitric oxide turns brown rapidly in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitric oxide is 25 parts of nitric oxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of nitric oxide per cubic meter of air (mg/m^3). NIOSH has recommended a permissible exposure limit of 25 ppm (30 mg/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Oxides of Nitrogen should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitric oxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Nitric oxide changes into nitrogen dioxide in air. Nitrogen dioxide is more toxic than nitric oxide and may cause severe breathing difficulties which may be delayed in onset. Nitrogen dioxide may also cause irritation of the eyes, nose, throat, and wet skin. Exposure of animals to nitric oxide has caused drowsiness, unconsciousness, and death.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitric oxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitric oxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, respiratory tract, and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Exposure to nitric oxide involves simultaneous exposure to nitrogen dioxide which causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Exposure to nitric oxide involves simultaneous exposure to nitrogen dioxide which is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or as otherwise indicated by the responsible physician.

- **Summary of toxicology**

Nitric oxide (NO) causes narcosis in animals. Exposure of mice to 2500 ppm for 6 or 7 minutes caused narcosis, and death occurred within 12 minutes. Some early reports attributed the toxicity of nitric oxide to the formation of methemoglobin; however, more recent studies indicate that nitric oxide reacts in vitro with normal (ferrous) hemoglobin but in exposed animals this interaction does not occur and no methemoglobin is

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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formed. Nitric oxide is converted spontaneously in air to nitrogen dioxide; hence, some of the latter gas is invariably present whenever nitric oxide is found in the air. At concentrations below 50 ppm, however, this reaction is slow, and frequently substantial concentrations of nitric oxide may occur with negligible quantities of nitrogen dioxide. Nitrogen dioxide may cause delayed pulmonary edema and irritation of the eyes, nose, throat, and wet skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 30
2. Boiling point (760 mm Hg): −152 C (-241 F)
3. Specific gravity (water = 1): 1.27 (at boiling point)
4. Vapor density (air = 1 at boiling point of nitric oxide): 1.0
5. Melting point: −164 C (−263 F)
6. Vapor pressure at 20 C (68 F): 26,000 mm Hg (500 psig, cylinder pressure)
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Contact with all combustible materials, chlorinated hydrocarbons, ammonia, carbon disulfide, many metals, fluorine, and ozone may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitric oxide decomposes.
4. Special precautions: Nitric oxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizing agent.

- **Warning properties**

1. Odor Threshold: May gives odor thresholds for nitric oxide of 0.3 ppm and 1 ppm.
2. Eye Irritation Level: According to Patty, nitric oxide is not an irritant. It is oxidized in air to NO_2, however, and NO_2 is known to produce eye irritation.
3. Evaluation of Warning Properties: Since the odor threshold of nitric oxide is well below the permissible exposure limit, nitric oxide is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Nitric oxide may be measured by the collection of nitric oxide on a solid sorbent, followed by extraction with triethanolamine and subsequent spectrophotometric analysis. Detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitric oxide may be used. An analytical method for nitric oxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitric oxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation of fumes caused by direct combination of nitrogen and oxygen at elevated temperatures; action of dilute nitric acid on some metals; oxidation of nitrogenous materials	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Use as an intermediate in synthesis of nitric acid, acrylonitrile, hydroxylamine, nitrosyl halides, nitrosyl hydrogen sulfate, nitrogen dioxide	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as decomposition agent in certain gaseous products; additive to rocket propellants; bleaching of rayon; laboratory research	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of nitric oxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If nitric oxide is leaked or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of leak or release to disperse the gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR NITRIC OXIDE

Condition	**Minimum Respiratory Protection* Required Above 25 ppm**
Gas Concentration	
100 ppm or less	Any chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxizidable sorbents and providing protection against nitric oxide.** A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against nitric oxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against nitric oxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Nitric oxide is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore and should not be used to provide protection against nitric oxide. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitric oxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for p-Nitroaniline

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_6N_2O_2$
- Synonyms: Azoic diazo component 37; para-nitroaniline; 4-nitroaniline; para-aminonitrobenzene; PNA; 1-amino-4-nitrobenzene; fast red 2G base; fast red GG base
- Appearance and odor: Yellow crystals with a pungent, faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-nitroaniline is 1 part of p-nitroaniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of p-nitroaniline per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Nitroaniline can affect the body if it comes in contact with the skin or eyes, is inhaled, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: p-Nitroaniline may cause a darkening or bluish coloring of the lips ("blue lip") and of the skin. Irritation of the nose and throat, headache, dizziness, weakness, nausea, shortness of breath, and rapid beating of the heart may occur. The overexposed person may become unconscious, cease breathing, and die.

2. Long-term Exposure: Prolonged overexposure may produce blue-colored lips and skin, and difficult breathing.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to p-nitroaniline.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-nitroaniline at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, liver, and cardiovascular system should be stressed.

—A complete blood count: p-Nitroaniline has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Liver function tests: Since liver damage has been observed in humans exposed to p-nitroaniline, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

p-Nitroaniline absorption, whether from inhalation of the vapor or absorption of the solid through skin, causes anoxia due to the formation of methemoglobin; jaundice and anemia have been reported. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, nose, and ear lobes, and is usually recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual usually feels well, has no complaints, and is insistent that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At concentrations of over 40% there usually is weakness and dizziness; up to a 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol aggravates the toxic effects of p-nitroaniline. The substance is mildly irritating to the eyes and may cause some corneal damage.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 138
2. Boiling point (760 mm Hg): 336 C (637 F)
3. Specific gravity (water = 1): 1.437
4. Vapor density (air = 1 at boiling point of p-nitroaniline): 4.76
5. Melting point: 146 C (293 F)
6. Vapor pressure at 20 C (68 F): 0.00015 mm Hg
7. Solubility in water, g/100 g water at 18.5 C (65 F): 0.08 (slight)
8. Evaporation rate (butyl acetate = 1): 22.6

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Strong oxidizers and moisture may result in spontaneous heating.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and carbon monoxide) may be released in a fire involving p-nitroaniline.
4. Special precautions: Liquid p-nitroaniline will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 199 C (390 F) (closed cup)
2. Autoignition temperature: 180 C (356 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical and carbon dioxide for small fires.

- **Warning properties**

1. Odor Threshold: The Manufacturing Chemists Association (MCA) states that p-nitroaniline is odorless.
2. Eye Irritation Level: p-Nitroaniline, according to the MCA, "is mildly irritating to the eyes and may cause some corneal damage." For the purposes of this guideline, quarter- and half-facepiece respirators are allowed up to 60 mg/m^3 (PF—10).
3. Evaluation of Warning Properties: Since the MCA states that p-nitroaniline is odorless and is only mildly irritating to the eyes, it is treated as a material with poor warning properties. The concentration in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- Method

An analytical method for p-nitroaniline is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid p-nitroaniline or liquids containing p-nitroaniline.
- If employees' clothing may have become contaminated with solid p-nitroaniline, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-nitroaniline should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of p-nitroaniline from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-nitroaniline, the person performing the operation should be informed of p-nitroaniline's hazardous properties.

- Where exposure of an employee's body to solid p-nitroaniline or liquids containing p-nitroaniline may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with p-nitroaniline should be removed immediately and not reworn until the p-nitroaniline is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid p-nitroaniline or liquids containing p-nitroaniline may contact the eyes.

SANITATION

- Skin that becomes contaminated with p-nitroaniline should be immediately washed or showered with soap or mild detergent and water to remove any p-nitroaniline.
- Workers subject to skin contact with solid p-nitroaniline should wash any areas of the body which may have contacted p-nitroaniline at the end of each work day.
- Eating and smoking should not be permitted in areas where solid p-nitroaniline is handled, processed, or stored.
- Employees who handle solid p-nitroaniline or liquids containing p-nitroaniline should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-nitroaniline may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use in synthesis and subsequent product preparation, such as grinding, containerization, etc.	Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection
Liberation during production of p-phenylenediamine; during production of intermediates for dyestuff manufacture; during antioxidation and antiozonation operations in rubber manufacture	Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection
Liberation during use as a gasoline-gum inhibitor; during use as an intermediate in pharmaceutical synthesis	Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If p-nitroaniline or liquids containing p-nitroaniline get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If p-nitroaniline or liquids containing p-nitroaniline get on the skin, immediately flush the contaminated skin with water. If p-nitroaniline or liquids containing p-nitroaniline soak through the clothing, remove the clothing immediately and flush the skin with water. If solid p-nitroaniline penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention as soon as possible.

- **Breathing**

If a person breathes in large amounts of p-nitroaniline, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When p-nitroaniline has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If p-nitroaniline is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

p-Nitroaniline may be disposed of:

1. By making packages of p-nitroaniline in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-nitroaniline in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR P-NITROANILINE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Particulate and Vapor Concentration	
60 mg/m³ (10 ppm) or less	Any supplied-air respirator. Any self-contained breathing apparatus.
300 mg/m³ (50 ppm) or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 300 mg/m³ (50 ppm) or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Nitrobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5NO_2$
- Synonyms: Nitrobenzol; oil of mirbane
- Appearance and odor: Pale yellow to dark brown, oily liquid with an odor like black paste shoe polish. It can be a solid at temperatures below 5.1 C (41 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrobenzene is 1 part of nitrobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of nitrobenzene per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrobenzene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It is readily absorbed through the skin, either as liquid or vapor. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

1. *Short-term Exposure:* Nitrobenzene affects the ability of blood to carry oxygen. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. Direct contact with the eyes or skin may cause mild irritation. Ingestion of alcohol may cause aggravation of symptoms.

2. *Long-term Exposure:* Repeated or prolonged exposure to nitrobenzene may cause anemia. An allergic skin rash may occur.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitrobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrobenzene at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, liver, kidneys, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Nitrobenzene has been shown to cause methemoglobinemia and may cause anemia. Those with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Observe for Heinz bodies.

—Urinalysis: The presence of p-nitrophenol and p-aminophenol in the urine is an indication of exposure to nitrobenzene.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrobenzene absorption, whether from inhalation of the vapor or absorption of the liquid through skin, causes anoxia due to the formation of methemoglobin; chronic exposure produces anemia. In rabbits given

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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subcutaneous injections of 0.75 g of nitrobenzene there was methemoglobin, sulfhemoglobin, Heinz body formation in erythrocytes, a marked decrease in hematocrit and hemoglobin levels, reticulocytosis, and mild damage to the liver and kidney. Vapor concentrations near 40 ppm resulted in intoxication of workers; exposure to vapor concentrations averaging 6 ppm caused headache and vertigo; small amounts of methemoglobin and sulfhemoglobin and some Heinz bodies were found in the blood. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, often recognized by fellow workers. Cyanosis often occurs when the methemogoblin concentration is 15% or more. The individual may feel well, have no complaints, and may insist that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At methemoglobin concentrations of over 40% there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol aggravates the toxic effects of nitrobenzene. p-Nitrophenol and p-aminophenol are metabolites of nitrobenzene, and their presence in the urine is an indication of exposure. Nitrobenzene is mildly irritating to the eyes; it may produce dermatitis due to primary irritation or sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 123.1
2. Boiling point (760 mm Hg): 211 C (412 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of nitrobenzene): 4.3
5. Melting point: 5.1 C (41 F)
6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.19
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with concentrated nitric acid or nitrogen tetroxide may cause fires and explosions. Contact with caustics and chemically active metals such as tin and zinc can cause evolution of much heat and fumes.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitrobenzene.
4. Special precautions: Liquid nitrobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 88 C (190 F) (closed cup)
2. Autoignition temperature: 482 C (900 F)
3. Flammable limits in air, % by volume: Lower: 1.8
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Stern and May report that the odor threshold of nitrobenzene is 1.9 ppm.
2. Eye Irritation Level: Browning states that nitrobenzene causes "only slight transient (eye) irritation." Grant states that "the most reliably established ocular effects are secondary to discoloration of the blood from methemoglobinemia, and consist of brown discoloration of the vessels of the fundus and the conjunctiva."
3. Evaluation of Warning Properties: Since the odor threshold of nitrobenzene is within twice the permissible exposure limits, nitrobenzene is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of nitrobenzene in an adsorption tube containing silica gel, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrobenzene may be used. An analytical method for nitrobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nitrobenzene.
- If employees' clothing has had any possibility of being contaminated with liquid nitrobenzene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with liquid nitrobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitrobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitrobenzene, the person performing the operation should be informed of nitrobenzene's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid nitrobenzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with nitrobenzene should be removed immediately and not reworn until the nitrobenzene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid nitrobenzene may contact the eyes.

SANITATION

- Skin that becomes contaminated with nitrobenzene should be immediately washed or showered with soap or mild detergent and water to remove any nitrobenzene.
- Workers subject to skin contact with liquid nitrobenzene should wash with soap or mild detergent and water any areas of the body which may have contacted nitrobenzene at the end of each work day.
- Eating and smoking should not be permitted in areas where liquid nitrobenzene is handled, processed, or stored.
- Employees who handle liquid nitrobenzene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of chemical intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in solvent refining of lubricating oils; use in production of intermediates in synthesis of rubber chemicals, photographic chemicals, explosives, liquid propellants, and pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent in specialized surface coatings; use as a solvent in organic synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Use as perfume in manufacture of toilet and household soaps; use in synthesis of insecticides and germicides	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid nitrobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid nitrobenzene gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid nitrobenzene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of nitrobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid nitrobenzene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid or solid nitrobenzene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. If in the solid form, allow to melt and handle as indicated in (2) above.

- Waste disposal methods:

Nitrobenzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR NITROBENZENE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
10 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
50 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitrobenzene; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

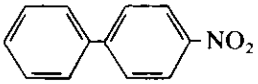
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
4-NITROBIPHENYL
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 4-nitrobiphenyl for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_9NO_2$
- **Structure:**



- **Synonyms:** p-Nitrobiphenyl; p-nitrodiphenyl; 4-nitrodiphenyl; p-phenyl-nitrobenzene; 4-phenylnitrobenzene; PNB
- **Identifiers:** CAS 92-93-3; RTECS DV560000; DOT not assigned
- **Appearance and odor:** White to yellow needle-like crystals with a sweetish odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 199.22
2. Boiling point (at 760 mmHg): 340°C (644°F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 4-nitrobiphenyl): 6.87
5. Melting point: 113.8°C (236.8°F)
6. Insoluble in water

- **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen) may be released in a fire involving 4-nitrobiphenyl.

- **Flammability**

1. Flash point: 143°C (290°F) (closed cup)
2. Extinguishant: Water or foam (may cause frothing)
3. Flammability Rating 1 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 4-nitrobiphenyl; however, the OSHA standard requires implementation of stringent controls wherever 4-nitrobiphenyl or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-nitrobiphenyl are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1003, 4-Nitrobiphenyl. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 4-nitrobiphenyl as an A1 substance (confirmed human carcinogen). The ACGIH recommends that virtually no exposure to 4-nitrobiphenyl be permitted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

4-Nitrobiphenyl may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Chronic oral administration of 4-nitrobiphenyl to dogs produced bladder cancer. In rats exposed to 4-nitrobiphenyl, the chemical is metabolically converted to 4-aminodiphenyl, a recognized animal and human bladder carcinogen.

2. *Effects on humans:* Because of the known metabolic conversion of 4-nitrobiphenyl to 4-aminodiphenyl in animals and the potential conversion in humans, it is not possible to separate the exposure to either substance; thus, the carcinogenicity of 4-nitrobiphenyl alone has not been documented in human epidemiologic studies. Bladder cancer is strongly associated

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with occupational exposure to 4-aminodiphenyl, and 4-nitrobiphenyl is used in the production of 4-aminodiphenyl.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 4-nitrobiphenyl can cause headache, lethargy, painful urination, and blood or pus in the urine.
2. *Long-term (chronic):* Exposure to 4-nitrobiphenyl can cause headache, weakness, dizziness, a feeling of euphoria, breathing difficulty (dyspnea), impaired muscular coordination (ataxia), blood or pus in the urine, and painful, difficult, or frequent urination.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 4-nitrobiphenyl, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 4-nitrobiphenyl. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver or urinary tract. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 4-nitrobiphenyl. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The physician should consider use of a test which characterizes internal exposure (e.g., benzidine in urine). However, this test should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 4-nitrobiphenyl may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include: Bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 4-nitrobiphenyl dust with glass fiber filters and silica gel tubes followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-nitrobiphenyl may also be used if available. A detailed sampling and analytical method for 4-nitrobiphenyl may be found in the *NIOSH Manual of Analytical Methods* (method number 273).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 4-nitrobiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting from a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 4-nitrobiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 4-nitrobiphenyl should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 4-nitrobiphenyl from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-nitrobiphenyl's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 4-nitrobiphenyl from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1003:

Areas where 4-nitrobiphenyl is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 4-nitrobiphenyl, local and systemic toxicity, the specific nature of the operation that could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 4-nitrobiphenyl which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-nitrobiphenyl into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-nitrobiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 4-nitrobiphenyl shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 4-nitrobiphenyl from materials, equipment, and the decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-nitrobiphenyl may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 4-nitrobiphenyl

Operations	Controls
During use in the production of rocket fuel; during use as an industrial solvent (especially in the fibers and plastics industries), as an oxidant, and as an additive in lubricants	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 4-nitrobiphenyl, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 4-nitrobiphenyl, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-nitrobiphenyl gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 4-nitrobiphenyl, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-nitrobiphenyl gets on the skin, wash it immediately with soap and water. If 4-nitrobiphenyl penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that areas affected by spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 4-nitrobiphenyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, 4-nitrobiphenyl may be collected and placed in an appropriate container.
4. 4-Nitrobiphenyl solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and mopping of 4-nitrobiphenyl are prohibited by OSHA. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.
5. For small quantities of liquids containing 4-nitrobiphenyl, absorb on paper towels and place in an appropriate container.
6. Large quantities of liquids containing 4-nitrobiphenyl may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 4-nitrobiphenyl

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for p-Nitrochlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $1,4\text{-}ClC_6H_4NO_2$
- Synonyms: PNCB; 4-chloronitrobenzene; PCNB; p-chloronitrobenzene; 1-chloro-4-nitrobenzene
- Appearance and odor: Yellow solid with a sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-nitrochlorobenzene is 1 milligram of p-nitrochlorobenzene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Nitrochlorobenzene can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed. It is readily absorbed through the skin. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

1. Short-term Exposure: p-Nitrochlorobenzene affects the ability of the blood to carry oxygen normally. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. p-Nitrochlorobenzene may also cause an unpleasant taste. The ingestion of alcohol may cause increased susceptibility to the effects of p-nitrochlorobenzene. The earliest effect may be a bluish color of the skin, especially of the lips. If the lack of oxygen becomes severe, drowsiness, headache, nausea, and vomiting may occur. If oxygen lack is very severe, it may cause unconsciousness and even death. It will also cause the mouth and breath to smell of bitter almonds.

2. Long-term Exposure: Repeated or prolonged exposure to p-nitrochlorobenzene may cause anemia and skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to p-nitrochlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-nitrochlorobenzene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, liver, kidneys, and cardiovascular system should be stressed.

—A complete blood count: p-Nitrochlorobenzene has been shown to cause methemoglobinemia and anemia. Those with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Observe for Heinz bodies.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Absorption of p-nitrochlorobenzene, whether by inhalation of vapor or dust or by absorption of the solid through the skin, causes anoxia due to the formation of methemoglobin. Application of the solid dissolved in

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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olive oil to the skin of rabbits caused methemoglobinemia, the formation of Heinz bodies in erythrocytes, anemia, hematuria, and hemoglobinuria. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and may be recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual may feel well, have no complaints, and may insist that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At methemoglobin concentrations of over 40% there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. The ingestion of alcohol aggravates the toxic effects of p-nitrochlorobenzene. Four workers exposed for a period of 2 to 4 days to an unmeasured concentration of the vapor developed methemoglobinemia; an unpleasant taste in mouth and anemia developed during the week after exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 157.6
2. Boiling point (760 mm Hg): 242 C (468 F)
3. Specific gravity (water = 1): 1.37
4. Vapor density (air = 1 at boiling point of p-nitrochlorobenzene): 5.4
5. Melting point: 83 C (181 F)
6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.003
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, hydrogen chloride, and carbon monoxide) may be released in a fire involving p-nitrochlorobenzene.
4. Special precautions: Liquid p-nitrochlorobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 127 C (261 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

According to Grant, nitrochlorobenzene (NCB), "like nitrobenzene, has been observed to cause methemoglobinemia, with discoloration of the conjunctiva reflecting the change in the color of the blood." NCB is not known to be an eye irritant, however.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of p-nitrochlorobenzene in an absorption tube containing silica gel, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure p-nitrochlorobenzene may be used. An analytical method for p-nitrochlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene, where skin contact may occur.
- If employees' clothing may have become contaminated with p-nitrochlorobenzene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-nitrochlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of p-nitrochlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-nitrochlorobenzene, the person performing the operation should be informed of p-nitrochlorobenzene's hazardous properties.
- Where exposure of an employee's body to liquids containing p-nitrochlorobenzene may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes wet with liquids containing p-nitrochlorobenzene should be removed immediately and not reworn until the p-nitrochlorobenzene is removed from the clothing.

SANITATION

- Skin that becomes wet with liquids containing p-nitrochlorobenzene should be immediately washed or showered with soap or mild detergent and water to remove any p-nitrochlorobenzene.
- Skin that becomes wet with p-nitrochlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any p-nitrochlorobenzene.
- Workers subject to skin contact with p-nitrochlorobenzene should wash with soap or mild detergent and water any areas of the body which may have contacted p-nitrochlorobenzene at the end of each work day.
- Eating and smoking should not be permitted in areas where p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene are handled, processed, or stored.
- Employees who handle p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-nitrochlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of chemical intermediates for manufacture of pesticides, fungicides, and preservatives; production of chemical intermediates for manufacture of sulfur and azo-fast dyes; synthesis of intermediates in manufacture of pharmaceuticals, rubber chemicals, antioxidants, gasoline gum inhibitors, corrosion inhibitors, and photographic chemicals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of p-nitrochlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If p-nitrochlorobenzene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

p-Nitrochlorobenzene may be disposed of:

1. By making packages of p-nitrochlorobenzene in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-nitrochlorobenzene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR p-NITROCHLOROBENZENE

Condition	**Minimum Respiratory Protection* Required Above 1 mg/m³**
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator, except single-use.
10 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Nitroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitroethane is 100 parts of nitroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 310 milligrams of nitroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

In man, mild skin irritation has occured from repeated exposure of the skin. Animal exposure to nitroethane has produced irritation of the respiratory tract with breathing difficulties which may be delayed in onset. Irritation of the eyes, anesthesia, and death have also occured.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from nitroethane exposure.

—Chronic respiratory disease: Nitroethane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of nitroethane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Nitroethane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Nitroethane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Nitroethane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Nitroethane is a mild skin irritant. In animals, nitroethane vapor is narcotic and a pulmonary irritant and also causes liver damage. Rabbits died from exposure to 5000 ppm for 3 hours; exposure to 2500 ppm for 3 hours was not fatal. Effects were lacrimation, dyspnea, pulmonary rales, and, in a few animals, pulmonary edema. Twitching and jerking movements of the head and extremities were observed; convulsions were rare and of brief duration. Stupor or narcosis at high concentra-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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tions was rapidly reversible. Autopsy of animals exposed to lethal concentrations showed mild to severe liver damage and non-specific changes in the kidneys. No systemic effects have been reported in humans. The liquid is a mild skin irritant due to solvent action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 75.1
2. Boiling point (760 mm Hg): 114 C (237 F)
3. Specific gravity (water = 1): 1.05
4. Vapor density (air = 1 at boiling point of nitroethane): 2.6
5. Melting point: −90 C (−130 F)
6. Vapor pressure at 20 C (68 F): 15.6 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 4.5
8. Evaporation rate (butyl acetate = 1): 1.2

- **Reactivity**

1. Conditions contributing to instability: Overheating of closed containers may cause detonation.

2. Incompatibilities: Contact with amines, strong acids, and alkalies may sensitize nitroethane so that it will readily explode. Contact with strong oxidizers may cause fires and explosions. Mixtures of nitroethane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metal oxides may cause decomposition and development of pressure.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitroethane.

4. Special precautions: Liquid nitroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 27.8 C (82 F) (closed cup)
2. Autoignition temperature: 414 C (778 F)
3. Flammable limits in air, % by volume: Lower: 3.4; Upper: Data not available
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Patty states that "the odors of nitroparaffins are easily detectable, and concentrations below 200 ppm are disagreeable to most observers. The odor and sensory symptoms are not dependable warning properties."

2. Eye Irritation Level: The AIHA *Hygienic Guide* states that the vapors of nitroethane "are noticeably irritating at concentrations above 100 ppm but cannot be relied upon for warning properties." At 500 ppm and above, strong eye (and respiratory tract) irritation has been observed in animals.

3. Evaluation of Warning Properties: Patty states that "the odor and sensory symptoms (of the nitroparaffins) are not dependable warning properties."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for nitroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid nitroethane.
- Clothing wet with liquid nitroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitroethane, the person performing the operation should be informed of nitroethane's hazardous properties.
- Any clothing which becomes wet with liquid nitroethane should be removed immediately and not reworn until the nitroethane is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid nitroethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid nitroethane should be promptly washed or showered with soap or mild detergent and water to remove any nitroethane.
- Employees who handle liquid nitroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in coatings and adhesives on cellulose esters and synthetic resins	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of organic dyes, insecticides, pesticides, nitroplasticizers, pharmaceuticals, and other organic chemicals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a propellant; as a reaction-media fluid; as an extraction solvent in petroleum fractionation; use as a recrystallization solvent	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid nitroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid nitroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid nitroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of nitroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid nitroethane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid nitroethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid nitroethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Liquid nitroethane may be disposed of by diluting with fuel oil and by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR NITROETHANE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Nitrogen Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: NO_2 and N_2O_4
- Synonyms: Nitrogen tetroxide; NTO; dinitrogen tetroxide; nitrogen peroxide
- Appearance and odor: Dark brown fuming liquid or gas with a pungent, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrogen dioxide is a ceiling of 5 parts of nitrogen dioxide per million parts of air (ppm) (*Federal Register*, Vol. 43, No. 237, pp. 57601-03, 8 December 1978). This may also be expressed as 9 milligrams of nitrogen dioxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 1 ppm (1.8 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Oxides of Nitrogen should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrogen dioxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to nitrogen dioxide may cause severe breathing difficulties which are usually delayed in onset and which may cause death. Recovery may be slow (2 to 3 weeks) with possible relapse and possible permanent lung damage. Pneumonia may occur. Irritation of the eyes, nose, throat, and wet skin may occur with acute exposures.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitrogen dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrogen dioxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory tract and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Nitrogen dioxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nitrogen dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or as otherwise indicated by the responsible physician.

- **Summary of toxicology**

Nitrogen dioxide gas is a respiratory irritant; it causes pulmonary edema and rarely, among survivors, bronchiolitis obliterans. Brief exposure of humans to concentrations of about 250 ppm causes cough, production of mucoid or frothy sputum, and increasing dyspnea. Within 1 to 2 hours the person may develop pulmonary edema with tachypnea, cyanosis, and fine crackles and wheezes throughout the lungs, and tachycardia. Alter-

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natively, there may be only increasing dyspnea and cough over several hours, the symptoms then gradually subside over a 2- to 3-week period. The condition may then enter a second stage of abruptly increasing severity; fever and chills precede a relapse with increasing dyspnea, cyanosis, and recurring pulmonary edema. Death may occur either in the initial or second stage of the disease; a severe second stage may follow a relatively mild initial stage. The subject who survives the second stage usually recovers over 2 to 3 weeks; however, some do not return to normal, but experience varying degrees of impaired pulmonary function. The radiographic features in the acute initial stage vary from normal to those of typical pulmonary edema; most reports mention a pattern of nodular shadows on the chest film at the outset. The roentgenogram may then clear, only to show miliary mottling as the second stage commences, progressing to the development of a confluent pattern. Results of pulmonary function tests in the acute stage show reduction in lung volume and diffusing capacity; similar findings are recorded in the second stage. Pathologic examination of the acute lesion shows extensive mucosal edema and inflammatory cell exudation. The delayed lesion shows the histologic appearance of bronchiolitis obliterans; small bronchi and bronchioles contain an inflammatory exudate which tends to undergo fibrinous organization, finally obliterating the lumen. The effects expected in humans from exposure to nitrogen dioxide for 60 minutes are: 100 ppm, pulmonary edema and death; 50 ppm, pulmonary edema with possible subacute or chronic lesions in the lungs; 25 ppm, respiratory irritation and chest pain. A concentration of 50 ppm is moderately irritating to the eyes and nose; 25 ppm is irritating to some people.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46 and 92
2. Boiling point (760 mm Hg): 21 C (70 F)
3. Specific gravity (water = 1): 1.45 (liquid)
4. Vapor density (air = 1 at boiling point of nitrogen dioxide): 2.83
5. Melting point: −11.2 C (11.8 F)
6. Vapor pressure at 20 C (68 F): 720 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions (reacts to form nitric acid and nitric oxide)
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to explode.
2. Incompatibilities: Contact with all combustible materials, chlorinated hydrocarbons, ammonia, and carbon disulfide may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitrogen dioxide decomposes.
4. Special precautions: Nitrogen dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizing agent.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* reports an odor threshold of 5 ppm.
2. Eye Irritation Level: According to Grant, "the gas at a concentration in approximately 70 ppm in air causes irritation of the eyes and nose evident in guinea pigs, rabbits, monkeys, and dogs during the first hour of exposure. At this concentration the gas has been lethal to most of the animals if exposed for eight hours, and under these conditions corneal opacities have been produced in the rabbits. The corneas of rabbits that survived such exposures did not improve under observation during twenty days. However, the gas at concentrations up to 20 ppm in air and exposure of four hours has produced no significant effect on the corneas of rabbits . . . . Exposure of the same magnitude repeated daily for more than a month also has not been damaging to the eye." The *Documentation of TLV's* reports that according to Patty, 10-20 ppm "were mildly irritant to the eyes . . . ."
3. Other Information: The AIHA *Hygienic Guide* states that "exposures of relatively short duration to concentrations above 5 ppm produce cough and irritation of the respiratory tract."
4. Evaluation of Warning Properties: Through its odor and irritant effects, nitrogen dioxide can be detected slightly above the recommended permissible exposure limit. For the purposes of this guideline, therefore, nitrogen dioxide is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of nitrogen dioxide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of gas in a reagent-filled impinger with a subsequent spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrogen dioxide may be used. An analytical method for nitrogen dioxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nitrogen dioxide.
- Clothing contaminated with nitrogen dioxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitrogen dioxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitrogen dioxide, the person performing the operation should be informed of nitrogen dioxide's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid nitrogen dioxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with nitrogen dioxide should be removed immediately and not reworn until the nitrogen dioxide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nitrogen dioxide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid nitrogen dioxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with nitrogen dioxide should be immediately washed or showered to remove any nitrogen dioxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrogen dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Use during metal surface treatment with nitric acid; in production of intermediates in manufacture of sulfuric acid, nitric acid, and fertilizers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation of fumes during engine maintenance, synthesis of dyes, manufacture of nitrocellulose paints, lacquers, and storage of silage in agricultural operations; production and handling of rocket propellants	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation of fumes during detonation of explosives	Personal protective equipment
Use in chemical synthesis during nitration operations	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid nitrogen dioxide or strong concentrations of nitrogen dioxide vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid nitrogen dioxide or strong concentrations of nitrogen dioxide vapor get on the skin, immediately flush the contaminated skin with water. If liquid nitrogen dioxide or strong concentrations of nitrogen dioxide vapor penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of nitrogen dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid nitrogen dioxide has been swallowed and if the person is conscious, immediately give the person large amounts of water to dilute the nitrogen dioxide. Do not attempt to make the unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nitrogen dioxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in the liquid form, allow to vaporize.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR NITROGEN DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
50 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxidizable sorbents and providing protection against nitrogen dioxide.** A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against nitrogen dioxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 50 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against nitrogen dioxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Nitrogen dioxide is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore should not be used to provide protection against nitrogen dioxide. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitrogen dioxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 50 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Nitrogen Trifluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: NF_3
- Synonyms: None
- Appearance and odor: Colorless gas with a moldy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrogen trifluoride is 10 parts of nitrogen trifluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 29 milligrams of nitrogen trifluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrogen trifluoride can affect the body if it is inhaled.

- **Effects of overexposure**

There are no reports of human intoxication from nitrogen trifluoride. In animals, nitrogen trifluoride can affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause a bluish discoloration of the skin, drowsiness, dizziness, nausea, rapid heart beat, headache, shortness of breath, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitrogen trifluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrogen trifluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, cardiovascular system, nervous system, liver, and kidneys should be stressed.

—A complete blood count: Nitrogen trifluoride has been shown to cause methemoglobinemia in animals. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrogen trifluoride gas causes anoxia due to the formation of methemoglobin in animals. Rats died from exposure to 10,000 ppm for 60 to 70 minutes; the methemoglobin concentrations at the time of death were equivalent to 60 to 70% of available hemoglobin. Animals exposed to nearly lethal concentrations suffered severe respiratory distress and cyanosis due to methemoglobinemia; severely affected animals showed incoordination, collapse and convulsions. Rats repeatedly exposed to 100 ppm for 4-½ months appeared normal, but autopsy findings indicated injury to the liver and kidneys. There are no reports of human intoxication from nitrogen trifluoride; however, the expected effects of methemoglobinemia in humans would result from anoxia and include cyanosis, evident

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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especially in the lips, nose, and ear lobes; other effects are weakness, dizziness, and severe headache.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 71
2. Boiling point (760 mm Hg): −129 C (−200 F)
3. Specific gravity (water = 1): 1.54 (liquid)
4. Vapor density (air = 1 at boiling point of nitrogen trifluoride): 2.5
5. Melting point: −206.8 C (−340 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Particularly hazardous under pressure; can react spontaneously due to shock or heat.
2. Incompatibilities: Contact of nitrogen trifluoride with oxidizable materials (such as ammonia, carbon monoxide, methane, hydrogen, and hydrogen sulfide), chemically active metals, and oxides (such as silica (sand)) may cause fires and explosions. Mixtures of nitrogen trifluoride and water vapor may explode when ignited by high energy sources. It can react violently with grease or oil.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible by itself, but can react explosively with reducing materials.
2. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, "NF_3 provides no odor-warning properties at potentially dangerous levels."
2. Eye Irritation Level: The ILO states that "nitrogen trifluoride is strikingly less irritating than elemental fluorine, chlorine trifluoride, and oxygen difluoride." Information is not available concerning the threshold of eye irritation.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of nitrogen trifluoride, and since the *Documentation of TLV's* states that "NF_3 provides no odor-warning properties at potentially dangerous levels," this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for nitrogen trifluoride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrogen trifluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of flash cubes; use in welding, brazing, and cutting of metals using hydrogen-nitrogen trifluoride torch	Process enclosure; local exhaust ventilation; personal protective equipment
Use in research as an oxidizer for rocket and other high-energy fuels	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of tetrafluorohydrazine	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of nitrogen trifluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If nitrogen trifluoride is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Nitrogen Trifluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR NITROGEN TRIFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
100 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against nitrogen trifluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR NITROGLYCERIN AND ETHYLENE GLYCOL DINITRATE

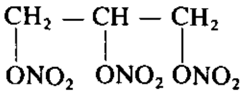
INTRODUCTION

This guideline summarizes pertinent information about nitroglycerin (NG) and ethylene glycol dinitrate (EGDN) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

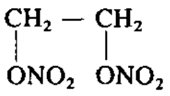
SUBSTANCE IDENTIFICATION

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate.

- **Formula:** (1) $C_3H_5N_3O_9$ (2) $C_2H_4N_2O_6$
- **Structure:**

(1) 

$\underset{ONO_2}{CH_2} - \underset{ONO_2}{CH} - \underset{ONO_2}{CH_2}$

(2) 

$\underset{ONO_2}{CH_2} - \underset{ONO_2}{CH_2}$

- **Synonyms:** (1) Anginine, blasting gelatin, blasting oil, glonoin, glycerol trinitrate, glyceryl nitrate, glyceryl trinitrate, GTN, myocon, NG, niglycon, niong, nitric acid triester of glycerol, nitrine-TDC, nitroglycerol, nitroglyn, nitrol; (2) Dinitroglycol, EGDN, ethanediol dinitrate, ethylene dinitrate, ethylene nitrate, glycol dinitrate, nitroglycol
- **Identifiers:** (1) CAS 55-63-0; RTECS QX2100000; DOT not assigned; (2) CAS 628-96-6; RTECS KW5600000; DOT not assigned
- **Appearance and odor:** (1) Pale yellow, slightly sweet smelling oil; (2) yellowish liquid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate. If not specified, data apply to both compounds.

- **Physical data**

1. Molecular weight: (1) 227.11; (2) 152.08
2. Boiling point (at 760 mmHg): (1) 256°C (493°F); (2) 197-200°C (387-392°F)
3. Explosive point: (1) 270°C (518°F); (2) 114°C (237°F)
4. Specific gravity (water = 1): (1) 1.6; (2) 1.49
5. Vapor density: (1) 7.8 (air = 1 at boiling point of NG); (2) 5.24 (air = 1 at boiling point of EGDN)
6. Melting point: (1) 13.1°C (55.1°F); (2) -22.3°C (-9°F)
7. Vapor pressure at 20°C (68°F): (1) 0.00012-0.011 mmHg; (2) 0.04 mmHg
8. (1) Slightly soluble in water; (2) insoluble in water

- **Reactivity**

1. Incompatibilities: Contact with acids, heat, or mechanical shock may result in explosion.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in an explosion involving NG or EGDN.

- **Flammability**

1. Flash point: Explodes
2. Autoignition temperature: (1) 270.4°C (518°F); (2) 195°C (383°F)
3. Class A Explosive (29 CFR 1910.109), Flammability Rating 2 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, NG and EGDN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for NG and EGDN is 0.2 parts of NG or EGDN per million parts of air (ppm) [2 milligrams of NG or 1 milligram of EGDN per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for NG or EGDN alone or for mixtures of the two substances is 0.1 mg/m³ as a ceiling concentration determined in any 20-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for NG or EGDN is

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Division of Standards Development and Technology Transfer

0.05 ppm (0.5 mg/m^3 NG or 0.3 mg/m^3 EGDN) as a time-weighted average concentration (TWA) for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational exposure limits for nitroglycerin and ethylene glycol dinitrate

	Exposure limits	
	ppm	mg/m^3
OSHA PEL		
NG ceiling (Skin)*	0.2	2
EGDN ceiling (Skin)†	0.2	1
NIOSH REL		
Ceiling (20 min)	—	0.1
ACGIH TLV®		
NG TWA (Skin)	0.05	0.5
EGDN TWA (Skin)	0.05	0.3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† If the atmospheric concentration of EGDN exceeds 0.02 ppm, personal protection may be necessary to avoid headache.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

NG and EGDN may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Subchronic inhalation of EGDN by mice caused lethargy, skin damage, muscle spasms, and death due to circulatory and respiratory paralysis. In cats, subchronic or chronic inhalation or dermal administration of EGDN caused severe anemia, decreased appetite, seizures, hemorrhage of internal organs, and death. Chronic oral administration of NG to rats produced cancer of the liver. NIOSH will continue to monitor the research regarding NG to determine whether the collective evidence justifies controlling this chemical as a carcinogen.
2. *Effects on humans:* Acute inhalation or dermal exposure of workers to NG and EGDN has caused decreased systolic, diastolic, and pulse blood pressures due to vascular dilation. Chronic exposure to NG and EGDN has caused damage to the heart and reduced tolerance to alcohol. Chronic exposure to NG and EGDN, or to NG alone, followed by a brief or extended period away from exposure, has been associated with an increased incidence of sudden death.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to NG and EGDN can cause severe headache, dizziness, nausea, and heart palpitations.
2. *Long-term (chronic):* Exposure to NG and EGDN can cause severe chest pain (angina pectoris), which frequently occurs during brief periods away from work. Skin sensitization can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to NG or EGDN, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and nervous, cardiovascular, and hematopoietic (blood-cell-forming) systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to NG or EGDN at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical or other findings suggestive of cardiovascular disease, especially coronary artery disease. The physician should obtain baseline values for electrocardiographic studies appropriate for the age and medical history of the worker.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to NG or EGDN. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and nervous, hematopoietic, and cardiovascular systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to NG or EGDN may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include methemoglobinemia.
2. Delayed-onset SHE's include methemoglobinemia and chest pain (angina pectoris).

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of NG and EGDN. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 20-minute sample or a series of consecutive samples that total 20 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting NG and EGDN vapors with tenax solid sorbent tubes followed by desorption with ethanol and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure NG and EGDN may also be used if available. A detailed sampling and analytical method for NG and EGDN may be found in the *NIOSH Manual of Analytical Methods* (method number 2507).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with NG and EGDN.

Workers should be provided with and required to use splash-proof safety goggles where NG or EGDN may come in contact with the eyes.

SANITATION

Clothing which is contaminated with NG or EGDN should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of NG and EGDN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of NG and EGDN's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with NG or EGDN should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle NG or EGDN should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to NG and EGDN may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for nitroglycerin and ethylene glycol dinitrate

Operations	Controls
During formulation and filling operations in the manufacture of industrial explosives and propellants	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the synthesis and handling of NG or EGDN; during the handling of industrial explosives	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the preparation and handling of dosage forms including tablets and solutions in the manufacture of pharmaceuticals	Process enclosure, local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to NG or EGDN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If NG or EGDN gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with these compounds.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to NG or EGDN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If NG or EGDN gets on the skin, wash it immediately with soap and water. If NG or EGDN penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If NG or EGDN is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing NG or EGDN, absorb on sponges or paper towels kept in a sodium carbonate solution. Remove paper towels to a secure outdoor location for burning.
4. Large quantities of liquids containing NG or EGDN may be washed with water into holding tanks where NG and EGDN can be separated. NG and EGDN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, NG and EGDN may be collected using nonsparking tools and removed to a secure, outdoor location for burning.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for nitroglycerin and ethylene glycol dinitrate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.2 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 0.5 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 2 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 20 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 40 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 40 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.1 mg/m^3 (ceiling).

Occupational Health Guideline for Nitromethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3NO_2
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitromethane is 100 parts of nitromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 250 milligrams of nitromethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitromethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

In man, mild skin irritation has occurred from repeated exposure of the skin. Animal exposure to nitromethane has produced irritation of the respiratory tract, with breathing difficulties which might be delayed in onset. Irritation of the eyes, anesthesia, convulsion, and death have also occurred.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitromethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from nitromethane exposure.

—Chronic respiratory disease: Nitromethane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of nitromethane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Nitromethane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Convulsive disorders: Nitromethane causes convulsions in animals. Persons with a history of such disorders may be more susceptible to the effects of this agent.

—Kidney disease: Nitromethane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Nitromethane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Nitromethane is a mild skin irritant due to its solvent action. In animals the vapor affects the central nervous system by causing convulsions and narcosis and is a mild pulmonary irritant. It also causes liver damage in animals. Rabbits died from exposure to 10,000 ppm for 6 hours; there was weakness, ataxia and muscular incoor-

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dination followed by convulsions after a latent period. This concentration for 3 hours was not fatal. Autopsy of animals exposed to lethal concentrations revealed focal necrosis in the liver and moderate kidney damage. Lower concentrations produced slight irritation of the respiratory tract, followed by mild narcosis, weakness, and salivation, but no evidence of eye irritation. However, a single monkey exposed to 1000 ppm for eight 6-hour exposures died. No systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 61
2. Boiling point (760 mm Hg): 101.2 C (214 F)
3. Specific gravity (water = 1): 1.14
4. Vapor density (air = 1 at boiling point of nitromethane): 2.1
5. Melting point: −29 C (−20 F)
6. Vapor pressure at 20 C (68 F): 27.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 9.5
8. Evaporation rate (butyl acetate = 1): 1.39

- **Reactivity**

1. Conditions contributing to instability: Overheating of closed containers may cause detonation.
2. Incompatibilities: Contact with amines, strong acids, and alkalies may sensitize nitromethane so that it will readily explode. Contact with strong oxidizers may cause fires and explosions. Mixtures of nitromethane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metallic oxides may cause decomposition and development of pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitromethane.
4. Special precautions: Liquid nitromethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 35 C (95 F) (closed cup)
2. Autoignition temperature: 418 C (785 F)
3. Flammable limits in air, % by volume: Lower: 7.3; Upper: Data not available
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, "the odor is very strong above 100 ppm and irritating at 200 ppm, but cannot be relied on for warning properties." No further explanation is offered. Patty also states, however, that "the odors of nitroparaffins are easily detectable, and concentrations below 200 ppm are disagreeable to most observers. The odor and sensory symptoms are not dependable warning properties."
2. Eye Irritation Level: The *Hygienic Guide* states that "severe eye and respiratory irritation was noted in animals at 500 ppm and above." This is not specifically stated to be the threshold of eye irritation.
3. Evaluation of Warning Properties: Patty states that "the odor and sensory symptoms (of nitroparaffins) are not dependable warning properties."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for nitromethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid nitromethane.
- Clothing wet with liquid nitromethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitromethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitromethane, the person performing the operation should be informed of nitromethane's hazardous properties.

- Any clothing which becomes wet with liquid nitromethane should be removed immediately and not reworn until the nitromethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid nitromethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid nitromethane should be promptly washed or showered to remove any nitromethane.
- Employees who handle liquid nitromethane should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in coatings and adhesives on cellulose esters and synthetic resins	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during application by dipping, roller coating, tumbling, knifing, or application of coatings and adhesives	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of organic dyes, textiles, surfactants, insecticides, pharmaceuticals, and explosives	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a propellant or fuel additive; use as a reaction-media fluid for Friedel-Crafts reaction; use as a recrystallization solvent; use as a solvent in manufacture of coatings and adhesives on cellulose esters or synthetic resins	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a stabilizer for halogenated alkanes, aerosol formulations, and paste formulations for inks	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid nitromethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid nitromethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid nitromethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of nitromethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid nitromethane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid nitromethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid nitromethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Liquid nitromethane may be disposed of by diluting with fuel oil and atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR NITROMETHANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1-Nitropropane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH_2CH_2NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1-nitropropane is 25 parts of 1-nitropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 90 milligrams of 1-nitropropane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for 1-nitropropane from 25 ppm to 15 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1-Nitropropane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1-Nitropropane causes irritation of the eyes and respiratory tract, headache, nausea, vomiting, and diarrhea.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1-nitropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1-nitropropane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1-nitropropane exposure.

—Chronic respiratory disease: 1-Nitropropane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1-nitropropane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 1-Nitropropane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 1-Nitropropane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1-Nitropropane vapor is an eye irritant and in animals causes mild respiratory irritation and severe liver damage. Rabbits died from exposure to 5,000 ppm for 3 hours, but 10,000 ppm for 1 hour was not lethal. Effects were conjunctival irritation, lacrimation, slow respiration with some rales, muscular incoordination, ataxia, and weakness. Autopsy of animals exposed to lethal concentrations revealed severe fatty infiltration of the liver and moderate kidney damage. Human volunteers exposed to over 100 ppm noted eye irritation. There are no reports of systemic effects in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Molecular weight: 89.1
2. Boiling point (760 mm Hg): 131.6 C (268 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of 1-nitropropane): 3.1
5. Melting point: −108 C (−162 F)
6. Vapor pressure at 20 C (68 F): 7.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.4
8. Evaporation rate (butyl acetate = 1): 0.8

- **Reactivity**

1. Conditions contributing to instability: Overheating in closed containers may cause violent explosion.
2. Incompatibilities: Even though no detonation of 1-nitropropane has been reported, contact with amines, strong acids, and alkalies may cause 1-nitropropane to become unstable. Contact with strong oxidizers may cause fires and explosions. Mixtures of 1-nitropropane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metal oxides may cause decomposition and development of pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving 1-nitropropane.
4. Special precautions: Liquid 1-nitropropane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 35.6 C (96 F) (closed cup)
2. Autoignition temperature: 420.6 C (789 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: Data not available
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor (of nitropropane) is detectable at 300 ppm but not at 80 ppm."
2. Eye Irritation Level: Grant states that "tests of nitropropane vapor on human volunteers have established that a sensation of eye irritation is noted at a concentration of 150 ppm in air."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of nitropropane are not within three times the permissible exposure limit, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for 1-nitropropane had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Clothing wet with liquid 1-nitropropane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1-nitropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1-nitropropane, the person performing the operation should be informed of 1-nitropropane's hazardous properties.
- Any clothing which becomes wet with liquid 1-nitropropane should be removed immediately and not reworn until the 1-nitropropane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 1-nitropropane may contact the eyes.

SANITATION

- Employees who handle liquid 1-nitropropane should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1-nitropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a thinner and solvent for cellulose compounds, lacquers, and dopes; in vinyl resins for industrial coatings and printing inks; in synthetic finish removers,; and for oil- and spirit-soluble dyes of molded plastics	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an extraction solvent for purification, separation, recrystallization, and recovery for natural and synthetic resins, tars, coating materials, fats, and oils	Local exhaust ventilation; personal protective equipment
Use as a reaction medium in polymer technology, as a catalyst, initiator, and solvent	Local exhaust ventilation; personal protective equipment
Use in organic chemical synthesis for preparation of amines, nitrated alcohols, and acids, and chloronitroparaffins	Local exhaust ventilation; personal protective equipment
Use in manufacture of explosives	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid 1-nitropropane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid 1-nitropropane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid 1-nitropropane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1-nitropropane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid 1-nitropropane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid 1-nitropropane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid 1-nitropropane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Liquid 1-nitropropane may be disposed of by diluting in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR 1-NITROPROPANE

Condition	**Minimum Respiratory Protection* Required Above 25 ppm**
Vapor Concentration	
150 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2300 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-NITROPROPANE

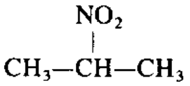
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 2-nitropropane for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_3H_7NO_2$
- **Structure:**



$CH_3-\overset{NO_2}{\overset{|}{C}}H-CH_3$

- **Synonyms:** Dimethylnitromethane; isonitropropane; 2-NP
- **Identifiers:** CAS 79-46-9; RTECS TZ5250000; DOT 2608, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless liquid with a fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 89.09
2. Boiling point (at 760 mmHg): 118°-120°C (244°-248°F)
3. Specific gravity (water = 1): 0.992
4. Vapor density (air = 1 at boiling point of 2-nitropropane): 3.07
5. Melting point: -93°C (-135°F)
6. Vapor pressure at 25°C (77°F): 20 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 1.7
8. Evaporation rate (butyl acetate = 1): 1.62
9. Saturation concentration in air (approximate) at 25°C (77°F): 2.6% (26,000 ppm)
10. Ionization potential: 10.71eV

- **Reactivity**

1. Incompatibilities: Contact with amines, strong acids, alkalies, or strong oxidizers may cause fire and explosion. Contact with some metal oxides may cause decomposition. Mixtures of 2-nitropropane and hydrocarbons are highly flammable.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 2-nitropropane.
3. Caution: Overheating 2-nitropropane in closed container may cause violent explosion. 2-Nitropropane will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 24°C (75°F) (closed cup)
2. Autoignition temperature: 428°C (802°F)
3. Flammable limits in air, % by volume: Lower, 2.6; upper, 11.0
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 3

- **Warning properties**

1. Odor threshold: 83 ppm
2. Eye irritation level: 150 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-nitropropane is 25 parts of 2-nitropropane per million parts of air (ppm) [90 milligrams of 2-nitropropane per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that 2-nitropropane be controlled and handled as a potential human carcinogen in the workplace; thus, the recommended exposure limit (REL) is that exposure be minimized to the lowest feasible level. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 2-nitropropane as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 10 ppm (35 mg/m^3) as TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for 2-nitropropane

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	25	90
NIOSH REL (Ca)*	Lowest feasible level	
ACGIH TLV® TWA (A2)†	10	35

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Nitropropane may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats, acute inhalation of 2-nitropropane caused progressive weakness, impaired muscular coordination (ataxia), and irregular breathing; in rats, rabbits, and guinea pigs, acute inhalation caused degeneration of the liver (necrosis), pulmonary edema and hemorrhage, selective destruction of brain cells, and vascular epithelial damage in all tissues. Subchronic inhalation of 2-nitropropane by rats produced an increased incidence of liver cancer. Intraperitoneal injection of 2-nitropropane in pregnant rats on days 1 through 15 of gestation caused retarded heart development in unborn fetuses.
2. *Effects on humans:* Acute inhalation exposure of workers to 2-nitropropane has produced toxic hepatitis, gastrointestinal bleeding, pulmonary edema, fatty degeneration and necrosis of the liver, and degeneration of kidney tubules; acute lethal exposure has also occurred. Chronic exposure of workers to 2-nitropropane has been associated with an increased incidence of lymphatic and connective tissue cancers.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to 2-nitropropane can cause nausea, vomiting, diarrhea, anorexia, severe headaches, breathing difficulty (dyspnea), impaired muscular coordination, and chest and abdominal pains.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 2-nitropropane, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-nitropropane. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic disease of the respiratory tract or liver. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. The physician should obtain baseline values for tests of liver function.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to 2-nitropropane. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires, tests of lung function, and chest X-rays.

- **Medical practices recommended at the time of job transfer or termination.**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 2-nitropropane may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting 2-nitropropane vapors with Chromosorb 106 tubes followed by desorption with ethyl acetate and analysis by gas chromatography. Direct-reading devices calibrated to measure 2-nitropropane may also be used if available. A detailed sampling and analytical method for 2-nitropropane may be found in the *NIOSH Manual of Analytical Methods* (method number 272).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with 2-nitropropane.

SANITATION

Clothing which is contaminated with 2-nitropropane should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 2-nitopropane from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-nitropropane's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with 2-nitropropane should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas. Workers who handle 2-nitropropane should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-nitropropane may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 2-nitropropane

Operations	Controls
During the manufacture and distribution of 2-nitropropane; during maintenance of equipment and storage containers for 2-nitropropane	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of explosives; during use as a thinner and solvent	Process enclosure, local exhaust ventilation, personal protective equipment
During use in organic chemical synthesis; during use as a propellant in rocket motors	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-nitropropane, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-nitropropane gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-nitropropane, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-nitropropane gets on the skin, wash it immediately with soap and water. If 2-nitropropane penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 2-nitropropane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing 2-nitropropane, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing 2-nitropropane may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing 2-nitropropane may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for 2-nitropropane

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

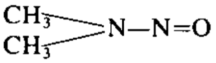
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR
N-NITROSODIMETHYLAMINE
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about N-nitrosodimethylamine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2H_6N_2O$
- **Structure:**



- **Synonyms:** Dimethylnitrosamine; N,N-dimethylnitrosamine; dimethylnitrosoamine; DMN; DMNA; N-methyl-N-nitrosomethanamine; NDMA; nitrosodimethylamine
- **Identifiers:** CAS 62-75-9; RTECS IQ0525000; DOT not assigned
- **Appearance and odor:** Yellow liquid of low viscosity

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.10
2. Boiling point (at 760 mmHg): 152 °C (305.6 °F)
3. Specific gravity (water = 1): 1.005
4. Vapor density (air = 1 at boiling point of N-nitrosodimethylamine): 2.56
5. Soluble in water

- **Reactivity**

1. Incompatibilities: Ultraviolet light; strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving N-nitrosodimethylamine.
3. Caution: Store in dark bottles.

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, or carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for N-nitrosodimethylamine; however, the OSHA standard requires implementation of stringent controls wherever N-nitrosodimethylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of N-nitrosodimethylamine are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1016, N-Nitrosodimethylamine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated N-nitrosodimethylamine as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

N-nitrosodimethylamine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute intraperitoneal injection of N-nitrosodimethylamine in rats produced cancer of the nasal cavity. In multiple species of animals, subchronic or chronic exposure via several routes of administration produced cancers of the liver, kidneys, or lungs. Intravenous or interplacental injections of N-nitrosodimethylamine in rats caused increased embryolethality and fetal mortality.
2. *Effects on humans:* Acute exposure of laboratory workers to N-nitrosodimethylamine has caused inflammation, degeneration, cirrhosis, and dysfunction of the liver and death.

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- **Signs and symptoms of exposure**

Short-term (acute): Exposure to N-nitrosodimethylamine can cause vomiting, abdominal cramps, diarrhea, headache, fever, and jaundice.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to N-nitrosodimethylamine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to N-nitrosodimethylamine. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to N-nitrosodimethylamine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity of and physiologic function of the liver, kidneys, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to N-nitrosodimethylamine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting N-nitrosodimethylamine vapors with Tenax GC in short glass tubes followed by desorption by heating and purging with helium, separation by capillary gas-liquid chromatography, and analysis by mass spectrometry. Direct-reading devices calibrated to measure N-nitrosodimethylamine may also be used if applicable. A detailed sampling and analytical method for N-nitrosodimethylamine may be found in the *NIOSH Manual of Analytical Methods* (method number 252).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where N-nitrosodimethylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where N-nitrosodimethylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with N-nitrosodimethylamine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of N-nitrosodimethylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of N-nitrosodimethylamine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove N-nitrosodimethylamine from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1016:

Areas where N-nitrosodimethylamine is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers are permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of N-nitrosodimethylamine, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving N-nitrosodimethylamine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of N-nitrosodimethylamine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where N-nitrosodimethylamine is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of N-nitrosodimethylamine shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove N-nitrosodimethylamine from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to N-nitrosodimethylamine may occur and control methods which may be effective in each case are listed in Table 1.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergen-

Table 1.—Operations and methods of control for N-nitrosodimethylamine

Operations	Controls
During use in the production of rocket fuel; during use as a solvent in the fibers and plastics industries, as an oxidant, and as an additive in lubricants	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substance

cy procedures. If a worker has contact with N-nitrosodimethylamine, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to N-nitrosodimethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If N-nitrosodimethylamine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to N-nitrosodimethylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If N-nitrosodimethylamine gets on the skin, wash it immediately with soap and water. If N-nitrosodimethylamine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If N-nitrosodimethylamine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities liquids containing N-nitrosodimethylamine, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing N-nitrosodimethylamine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. Liquids containing N-nitrosodimethylamine may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for N-nitrosodimethylamine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Nitrotoluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Ortho: 2-$NO_2C_6H_4CH_3$; Meta: 3-$NO_2C_6H_4CH_3$; Para: 4-$NO_2C_6H_4CH_3$
- Synonyms: Orthonitrotoluene; o-nitrotoluol; metanitrotoluene; m-nitrotoluol; paranitrotoluene; p-nitrotoluol
- Appearance and odor: Ortho: Yellow liquid or solid with a weak aromatic odor; Meta: Yellow liquid or solid with a weak aromatic odor; Para: Pale yellow solid with a weak aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrotoluene is 5 parts of nitrotoluene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of nitrotoluene per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for nitrotoluene from 5 ppm to 2 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrotoluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It is readily absorbed through the skin.

- **Effects of overexposure**

Nitrotoluene may affect the ability of the blood to carry oxygen. This may cause a bluish discoloration of the skin, irritability, drowsiness, nausea, rapid pulse, headache, weakness, shortness of breath, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitrotoluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrotoluene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, nervous system, gastrointestinal system, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Nitrotoluene has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrotoluene, whether absorbed as vapor by inhalation or as liquid through the skin, has a potential for producing methemoglobin and subsequent anoxia. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. The onset of symptoms of methemoglobinemia is insidious and may be delayed up to 4 hours; headache is commonly the

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis occurs when the methemoglobin concentration is 15% or more. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is usually recognized by fellow workers. Until the methemoglobin concentration approaches approximately 40%, the individual usually feels well, has no complaints, and will insist that nothing is wrong. At methemoglobin concentrations of over 40%, there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 137.1
2. Boiling point (760 mm Hg): Ortho: 222 C (432 F); Meta: 232 C (450 F); Para: 238 C (460 F)
3. Specific gravity (water = 1): Ortho: 1.16; Meta: 1.16; Para: 1.3
4. Vapor density (air = 1 at boiling point of nitrotoluene): 4.7
5. Melting point: Ortho: −4 C (25 F); Meta: 16 C (61 F); Para: 52 C (126 F)
6. Vapor pressure at 20 C (68 F): Ortho and Meta: 0.15 mm Hg; Para: 0.12 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.06; Meta: 0.05; Para: 0.004
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers or sulfuric acid may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitrotoluene.
4. Special precautions: Nitrotoluene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Ortho: 106 C (223 F) (closed cup); Meta: 101 C (214 F); Para: 106 C (223 F)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: Ortho: 2.2 (calculated); Meta and para: 1.6 (calculated)
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: Information is not available.
2. Eye Irritation Level: Nitrotoluene is not known to be an eye irritant.
3. Evaluation of Warning Properties: This substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using a silica gel adsorption tube with subsequent desorption using methanol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrotoluene may be used. An analytical method for nitrotoluene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid nitrotoluene.
- Non-impervious clothing which becomes contaminated with nitrotoluene should be removed promptly and not reworn until the nitrotoluene is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid nitrotoluene may contact the eyes.

SANITATION

- Skin that becomes contaminated with nitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any nitrotoluene.
- Eating and smoking should not be permitted in areas where solid nitrotoluene is handled, processed, or stored.
- Employees who handle solid or liquid nitrotoluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluidines for the production of dyes, intermediates for vulcanization accelerators, gasoline inhibitors, and flotation agents; use as an analytical reagent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in the manufacture of dinitrotoluenes for production of explosives; manufacture of nitrotoluene-sulfonic acids for production of azo and stilbene dyes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for intermediates of dyes, sun screening agents, and fuchsin— a red dye used in textile and leather industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid or liquid nitrotoluene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid nitrotoluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid nitrotoluene penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately

- **Breathing**

If a person breathes in large amounts of nitrotoluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solid or liquid nitrotoluene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nitrotoluene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquid nitrotoluene, absorb on paper towels. For small quantities of solid nitrotoluene, sweep onto paper or other suitable material. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities of liquid nitrotoluene can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Large quantities of solid nitrotoluene can be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Nitrotoluene may be disposed of:

1. For liquid nitrotoluene, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing liquid nitrotoluene in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By making packages of solid nitrotoluene in paper or

other suitable material or by dissolving in a flammable solvent (such as alcohol) and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Nitrotoluene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Baskin, A. D. (ed.): *Handling Guide for Potentially Hazardous Commodities*, Railway Systems and Management Association, Chicago, 1972.
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RESPIRATORY PROTECTION FOR NITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 ppm or 280 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
200 ppm or 1120 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 200 ppm or 1120 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Nitrotoluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Ortho: 2-$NO_2C_6H_4CH_3$; Meta: 3-$NO_2C_6H_4CH_3$; Para: 4-$NO_2C_6H_4CH_3$
- Synonyms: Orthonitrotoluene; o-nitrotoluol; metanitrotoluene; m-nitrotoluol; paranitrotoluene; p-nitrotoluol
- Appearance and odor: Ortho: Yellow liquid or solid with a weak aromatic odor; Meta: Yellow liquid or solid with a weak aromatic odor; Para: Pale yellow solid with a weak aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrotoluene is 5 parts of nitrotoluene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of nitrotoluene per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for nitrotoluene from 5 ppm to 2 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrotoluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It is readily absorbed through the skin.

- **Effects of overexposure**

Nitrotoluene may affect the ability of the blood to carry oxygen. This may cause a bluish discoloration of the skin, irritability, drowsiness, nausea, rapid pulse, headache, weakness, shortness of breath, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitrotoluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrotoluene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, nervous system, gastrointestinal system, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Nitrotoluene has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrotoluene, whether absorbed as vapor by inhalation or as liquid through the skin, has a potential for producing methemoglobin and subsequent anoxia. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. The onset of symptoms of methemoglobinemia is insidious and may be delayed up to 4 hours; headache is commonly the

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first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis occurs when the methemoglobin concentration is 15% or more. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is usually recognized by fellow workers. Until the methemoglobin concentration approaches approximately 40%, the individual usually feels well, has no complaints, and will insist that nothing is wrong. At methemoglobin concentrations of over 40%, there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 137.1
  2. Boiling point (760 mm Hg): Ortho: 222 C (432 F); Meta: 232 C (450 F); Para: 238 C (460 F)
  3. Specific gravity (water = 1): Ortho: 1.16; Meta: 1.16; Para: 1.3
  4. Vapor density (air = 1 at boiling point of nitrotoluene): 4.7
  5. Melting point: Ortho: −4 C (25 F); Meta: 16 C (61 F); Para: 52 C (126 F)
  6. Vapor pressure at 20 C (68 F): Ortho and Meta: 0.15 mm Hg; Para: 0.12 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.06; Meta: 0.05; Para: 0.004
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers or sulfuric acid may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitrotoluene.
  4. Special precautions: Nitrotoluene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Ortho: 106 C (223 F) (closed cup); Meta: 101 C (214 F); Para: 106 C (223 F)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: Ortho: 2.2 (calculated); Meta and para: 1.6 (calculated)
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: Information is not available.
  2. Eye Irritation Level: Nitrotoluene is not known to be an eye irritant.
  3. Evaluation of Warning Properties: This substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using a silica gel adsorption tube with subsequent desorption using methanol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrotoluene may be used. An analytical method for nitrotoluene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid nitrotoluene.
- Non-impervious clothing which becomes contaminated with nitrotoluene should be removed promptly and not reworn until the nitrotoluene is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid nitrotoluene may contact the eyes.

SANITATION

- Skin that becomes contaminated with nitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any nitrotoluene.
- Eating and smoking should not be permitted in areas where solid nitrotoluene is handled, processed, or stored.
- Employees who handle solid or liquid nitrotoluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluidines for the production of dyes, intermediates for vulcanization accelerators, gasoline inhibitors, and flotation agents; use as an analytical reagent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in the manufacture of dinitrotoluenes for production of explosives; manufacture of nitrotoluene-sulfonic acids for production of azo and stilbene dyes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for intermediates of dyes, sun screening agents, and fuchsin— a red dye used in textile and leather industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid or liquid nitrotoluene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid nitrotoluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid nitrotoluene penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately

- **Breathing**

If a person breathes in large amounts of nitrotoluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solid or liquid nitrotoluene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nitrotoluene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquid nitrotoluene, absorb on paper towels. For small quantities of solid nitrotoluene, sweep onto paper or other suitable material. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities of liquid nitrotoluene can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Large quantities of solid nitrotoluene can be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Nitrotoluene may be disposed of:

1. For liquid nitrotoluene, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing liquid nitrotoluene in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By making packages of solid nitrotoluene in paper or

other suitable material or by dissolving in a flammable solvent (such as alcohol) and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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Condition	Minimum Respiratory Protection* Required Above 5 ppm
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Greater than 200 ppm or 1120 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Nitrotoluene may affect the ability of the blood to carry oxygen. This may cause a bluish discoloration of the skin, irritability, drowsiness, nausea, rapid pulse, headache, weakness, shortness of breath, and unconsciousness.

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—A complete blood count: Nitrotoluene has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrotoluene, whether absorbed as vapor by inhalation or as liquid through the skin, has a potential for producing methemoglobin and subsequent anoxia. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. The onset of symptoms of methemoglobinemia is insidious and may be delayed up to 4 hours; headache is commonly the

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  7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.06; Meta: 0.05; Para: 0.004
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers or sulfuric acid may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitrotoluene.
  4. Special precautions: Nitrotoluene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Ortho: 106 C (223 F) (closed cup); Meta: 101 C (214 F); Para: 106 C (223 F)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: Ortho: 2.2 (calculated); Meta and para: 1.6 (calculated)
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: Information is not available.
  2. Eye Irritation Level: Nitrotoluene is not known to be an eye irritant.
  3. Evaluation of Warning Properties: This substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

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PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid nitrotoluene.
- Non-impervious clothing which becomes contaminated with nitrotoluene should be removed promptly and not reworn until the nitrotoluene is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid nitrotoluene may contact the eyes.

SANITATION

- Skin that becomes contaminated with nitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any nitrotoluene.
- Eating and smoking should not be permitted in areas where solid nitrotoluene is handled, processed, or stored.
- Employees who handle solid or liquid nitrotoluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrotoluene may occur and control methods which may be effective in each case:

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Use in the manufacture of toluidines for the production of dyes, intermediates for vulcanization accelerators, gasoline inhibitors, and flotation agents; use as an analytical reagent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in the manufacture of dinitrotoluenes for production of explosives; manufacture of nitrotoluene-sulfonic acids for production of azo and stilbene dyes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for intermediates of dyes, sun screening agents, and fuchsin— a red dye used in textile and leather industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid or liquid nitrotoluene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid nitrotoluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid nitrotoluene penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately

- **Breathing**

If a person breathes in large amounts of nitrotoluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solid or liquid nitrotoluene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If nitrotoluene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquid nitrotoluene, absorb on paper towels. For small quantities of solid nitrotoluene, sweep onto paper or other suitable material. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities of liquid nitrotoluene can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Large quantities of solid nitrotoluene can be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Nitrotoluene may be disposed of:

1. For liquid nitrotoluene, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing liquid nitrotoluene in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By making packages of solid nitrotoluene in paper or

other suitable material or by dissolving in a flammable solvent (such as alcohol) and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR NITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 ppm or 280 mg/m^3 or less	Any supplied-air respirator.
	Any self-contained breathing apparatus.
200 ppm or 1120 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 200 ppm or 1120 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Octachloronaphthalene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}Cl_8$
- Synonyms: Halowax 1051
- Appearance and odor: Pale, yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for octachloronaphthalene is 0.1 milligram of octachloronaphthalene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Octachloronaphthalene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Overexposure to octachloronaphthalene may cause an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, yellow jaundice, and possibly death.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to octachloronaphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to octachloronaphthalene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Octachloronaphthalene may cause liver damage. A profile of liver function should be performed by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Octachloronaphthalene may be regarded, mainly by analogy to the lower chlorinated naphthalenes such as the penta- and hexachlor derivatives, as probably toxic to the liver and the skin. There is no information on the effects of inhalation of vapor or dust on man. Ingestion experiments on cattle suggest that the octachlor is more toxic but less readily absorbed than the hexachlor derivative. Exposure of workers by inhalation or skin absorption to mixtures of chlorinated naphthalenes with a lower chlorine content has caused a severe acne-form dermatitis termed chloracne, as well as serious liver injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 403.7
2. Boiling point (760 mm Hg): 410 C (770 F) (approximately)
3. Specific gravity (water = 1): 2.0
4. Vapor density (air = 1 at boiling point of octachloronaphthalene): 13.9

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5. Melting point: 185 C (365 F)

6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and toxic chloride fumes) may be released in a fire involving octachloronaphthalene.

4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "eye injury has not proved to be troublesome with the chloronaphthalenes."

3. Evaluation of Warning Properties: There are no quantitative data relating warning properties to air concentrations of octachloronaphthalene; therefore, this substance is treated as a material with poor warning properties. The concentration of octachloronaphthalene in saturated air at 20 C could present a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of octachloronaphthalene on a filter, followed by extraction with hexane, and gas chromatographic analysis. An analytical method for octachloronaphthalene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten octachloronaphthalene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid octachloronaphthalene or liquids containing octachloronaphthalene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with octachloronaphthalene vapors from the heated material.
- If employees' clothing may have become contaminated with solid octachloronaphthalene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with octachloronaphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of octachloronaphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the octachloronaphthalene, the person performing the operation should be informed of octachloronaphthalene's hazardous properties.
- Non-impervious clothing which becomes contaminated with molten octachloronaphthalene should be removed immediately and not reworn until the octachloronaphthalene is removed from the clothing.
- Non-impervious clothing which becomes contaminated with solid octachloronaphthalene or liquids containing octachloronaphthalene should be removed promptly and not reworn until the octachloronaphthalene is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten octachloronaphthalene contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where solid octachloronaphthalene or liquids containing octachloronaphthalene may contact the eyes.

SANITATION

- Workers subject to skin contact with octachloronaphthalene should wash with soap or mild detergent and water any areas of the body which may have contacted octachloronaphthalene at the end of each work day.
- Skin that becomes contaminated with octachloronaphthalene should be promptly washed or showered with soap or mild detergent and water to remove any octachloronaphthalene.
- Eating and smoking should not be permitted in areas where solid octachloronaphthalene is handled, processed, or stored.
- Employees who handle solid octachloronaphthalene or liquids containing octachloronaphthalene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to octachloronaphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture of electric equipment as an insulating material; pouring molten solvent or finely ground solid materials; dipping; peeling and covering insulated cable with fabric	Local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Liberation from use of electrical equipment insulated with octachloronaphthalene/pentachloronaphthalene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an inert compound of resins or polymers for coating or impregnating textiles, wood, and paper to impart flame resistance, water proofness, and fungicidal and insecticidal properties	Process enclosure; local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Use as an additive for cutting oil in various operations performed on metals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive to special lubricants in crankcase oil, lubricants for farm machinery, and extreme-pressure lubricants	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid octachloronaphthalene or liquids containing octachloronaphthalene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. If molten octachloronaphthalene gets into the eyes, immediately flush the eyes with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If non-impervious clothing becomes contaminated with octachloronaphthalene, remove and clean the clothing before wearing it again. If non-impervious clothing becomes heavily contaminated, it should be destroyed. If solid octachloronaphthalene or liquids containing octachloronaphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If skin irritation persists after washing, get medical attention. If molten octachloronaphthalene gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of octachloronaphthalene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When octachloronaphthalene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If octachloronaphthalene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing octachloronaphthalene should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Octachloronaphthalene may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Octachloronaphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR OCTACHLORONAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m^3
Particulate Concentration	
1 mg/m^3 or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Octane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_8H_{18}
- Synonyms: Normal octane
- Appearance and odor: Colorless liquid with a gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for octane is 500 parts of octane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2350 milligrams of octane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm (350 mg/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 385 ppm (1800 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Octane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to octane may cause irritation of the eyes, nose, and skin, and drowsiness. Exposure to higher air concentrations may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to octane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to octane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Octane is a skin defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although octane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although octane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of octane might cause exacerbation of symptoms due to its irritant properties.

*2. Periodic Medical Examination:*The aforementioned medical examinations should be performed on an annual basis.

- **Summary of toxicology**

Octane vapor is a mild narcotic and mucous membrane irritant. Mice exposed at concentrations of 6600 to 13,700 ppm demonstrated signs of narcosis in 30 to 90 minutes. The narcotic concentration is approximately 8000 ppm, while the fatal concentration for animals is

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near 13,500 ppm. Repeated or prolonged skin contact with the liquid results in drying and cracking skin due to defatting action. No chronic systemic effects have been reported in humans. Aspiration may cause chemical pneumonia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 114.2
  2. Boiling point (760 mm Hg): 126 C (258 F)
  3. Specific gravity (water = 1): 0.7
  4. Vapor density (air = 1 at boiling point of octane): 3.9
  5. Melting point: −56.7 C (−70 F)
  6. Vapor pressure at 20 C (68 F): 11 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.04 (approximately)
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving octane.
  4. Special precautions: Octane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 13.3 C (56 F) (closed cup)
  2. Autoignition temperature: 220 C (428 F)
  3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 6.5
  4. Extinguishant: Foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Summer and May both report an odor threshold of 150 ppm for octane.
  2. Eye Irritation Level: According to the *Handbook of Organic Industrial Solvents*, "irritation occurs as exposure exceeds threshold limit."
  3. Evaluation of Warning Properties: Because of its low thresholds of odor and irritation, octane is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of octane. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of octane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure octane may be used. An analytical method for octane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid octane.
- Any clothing which becomes wet with liquid octane should be removed immediately and not reworn until the octane is removed from the clothing.
- Clothing wet with liquid octane should be placed in closed containers for storage until it can be discarded or

until provision is made for the removal of octane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the octane, the person performing the operation should be informed of octane's hazardous properties.

- Employees should be provided with and required to use splash-proof safety goggles where liquid octane may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to octane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid octane should be promptly washed or showered with soap or mild detergent and water to remove any octane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to octane may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of gasoline, rocket fuel, and of fuel cells, and in combustion studies	General dilution ventilation; local exhaust ventilation
Use as an industrial solvent as lacquer diluent, phosphate manufacture, and preparation of liquid soaps and detergents	General dilution ventilation; local exhaust ventilation
Use in azeotropic mixtures for printing ink manufacture, and separation distillation	General dilution ventilation; local exhaust ventilation
Use as an additive and solvent in polymer manufacture	General dilution ventilation; local exhaust ventilation
Use in manufacture of benzene, toluene, and xylene aromatics	Process enclosure; local exhaust ventilation; personal protective equipment
Use in laboratory procedures and studies	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a blowing agent for foam rubber used in rocket propellants	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If octane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If octane gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If octane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of octane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If octane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If octane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Octane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Octane may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR OCTANE

Condition	**Minimum Respiratory Protection* Required Above 500 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Mineral Oil Mist

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_nH_{2n+2} where n = 16 and up
- Synonyms: The mist of petroleum-based: white mineral oil; cutting oils; heat-treating oils; hydraulic oils; cable oil; transformer oil; lubricating oils; drawing oils
- Appearance and odor: Mist with an odor like burned lube oil generated from petroleum-base or white mineral petroleum oil.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mineral oil mist is 5 milligrams of mineral oil mist per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mineral oil mist can affect the body if it is inhaled.

- **Effects of overexposure**

Inhalation of mineral oil mist may cause adverse respiratory effects.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to mineral oil mist.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to mineral oil mist at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from mineral oil mist exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of mineral oil mist might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Prolonged exposure to mineral oil mist may cause a dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Inhalation of mineral oil mist in high concentrations may cause pulmonary effects, although this has rarely been reported. A single case of lipoid pneumonitis suspected to have been caused by exposure to very high concentrations of oil mist was reported in 1950; this occurred in a cash register serviceman, whose heavy exposure occurred over 17 years of employment; no other cases have been recorded. Experimental animal exposure studies to white mineral oil mist (untreated, and with no additions) for repeated daily 6-hour exposures for 1 year at 5 mg/m^3 were entirely negative in all criteria used for measuring response. A similar study at 100 mg/m^3 resulted in some slight changes in some but not all species exposed; no histologic changes of significance were noted. Exposure to oil mist did not appear to accelerate the production of lung tumors in a lung-tumor-susceptible strain of mice. A second parallel study of sulfurized, solvent-extracted naphthenic-base oil to which animals were exposed daily at 50 mg/m^3 for 18 months failed to reveal a single animal with any sort of injury or indisposition as a result of the oil mist inhalation. A review of exposures to mineral oil mist averaging 15 mg/m^3 (but often higher) in several industries disclosed a striking lack of reported cases of illness related to these exposures. A study of oil mist

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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exposures in machine shops, at mean concentrations of 3.7 mg/m^3 and maximum of 110 mg/m^3, showed no increase in respiratory symptoms or decrement in respiratory performance attributable to oil mist inhalation among men employed for many years. There is no evidence to suggest any relation between in- halation of oil mist and lung cancer. On the other hand, there are some reported cases of skin cancer from contact with certain oils. Contact with liquid oils may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: Not pertinent
  2. Boiling point (760 mm Hg): 360 C (680 F)
  3. Specific gravity (water = 1): 0.8 – 0.9
  4. Vapor density (air = 1 at boiling point of mineral oil mist): Not applicable
  5. Melting point: Very low
  6. Vapor pressure at 20 C (68 F): Very low
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Flash point: 135 C (275 F) (closed cup)
  2. Autoignition temperature: 260 – 371 C (500 – 700 F)
  3. Flammable limits in air, % by volume: Not applicable
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**

Mineral oil mist is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of mineral oil mist on a filter, followed by treatment with chloroform and analysis by fluorescence spectrophotometry. An analytical method for mineral oil mist is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid mineral oil.
- Non-impervious clothing which becomes wet with liquid mineral oil should be removed promptly and not reworn until the mineral oil mist is removed from the clothing.

SANITATION

- Skin that becomes wet with liquid mineral oil should be promptly washed or showered with soap or mild detergent and water to remove any mineral oil mist.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to mineral oil mist may occur and control methods which may be effective in each case:

Operation	Controls
Use as a coolant or quenching agent in machine shop operations and metal fabrication; during coating and cleaning in foundry operations	Process enclosure; local exhaust ventilation; general mechanical ventilation
Use in steel rolling operations; use in lubricating and cleaning of machinery	Process enclosure; local exhaust ventilation; general mechanical ventilation
Use in pressroom operations in printing	Mist suppression; local exhaust ventilation; general mechanical ventilation
Use in mine drilling operations	Process enclosure; local exhaust ventilation; general mechanical ventilation
Use as an insecticide	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Skin Exposure**

If skin becomes wet with mineral oil mist, wash the contaminated skin using soap or mild detergent and water. If mineral oil mist penetrates through the clothing, remove the clothing and wash the skin using soap or mild detergent and water.

- **Breathing**

If a person breathes in large amounts of mineral oil mist, move the exposed person to fresh air at once.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If mineral oil mist is released in hazardous concentrations, ventilate area of release to disperse the mist.
- If mineral oil mist is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

- Waste disposal methods:

Mineral oil mist may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR MINERAL OIL MIST

Condition	**Minimum Respiratory Protection*** **Required Above 5 mg/m^3**
Particulate Concentration	
25 mg/m^3 or less	Any mist respirator, except single-use.
50 mg/m^3 or less	Any mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2,500 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 2,500 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Osmium Tetroxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: OsO_4
- Synonyms: Osmic acid
- Appearance and odor: Colorless to pale yellow solid with a sharp, choking, chlorine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for osmium tetroxide is 0.002 milligrams of osmium tetroxide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for osmium tetroxide a Threshold Limit Value of 0.0002 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Osmium tetroxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to osmium tetroxide may cause severe eye damage accompanied by irritation with tearing. This may occur several hours after exposure has ceased. After exposure, halos may be seen around lights. Exposure to osmium tetroxide may also cause severe irritation of the nose, throat, and bronchial tubes with cough, wheezing, shortness of breath, and pneumonia. In addition, exposure to this chemical may also cause skin burns, skin rash, skin discoloration, and kidney damage.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to osmium tetroxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to osmium tetroxide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from osmium tetroxide exposure.

—Eye disease: Osmium tetroxide is an eye irritant and in workers has caused symptoms and signs of keratitis epithelia with corneal edema. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of osmium tetroxide might cause exacerbation of symptoms due to its irritant properties.

—Kidney disease: Osmium tetroxide causes mild kidney damage in animals. Persons with pre-existing kidney disease may be more susceptible to the effects of this agent.

—Skin disease: Osmium tetroxide is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Osmium tetroxide as dust or vapor is a severe irritant of the eyes and respiratory tract. Rabbits exposed for 30 minutes to vapor at estimated concentrations of 130 mg/m^3 developed irritation of mucous membranes and labored breathing; at autopsy there was bronchopneumonia, as well as slight kidney damage. A laboratory investigator exposed to a high concentration of vapor experienced a sensation of chest constriction and diffi-

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culty in breathing. Irritation of the eyes is usually the first symptom of exposure to low concentrations of the vapor; lacrimation, a gritty feeling in the eyes, and the appearance of rings around lights are frequently reported; in most cases, recovery occurs within a few days. Workers exposed to fume concentrations up to 0.6 mg/m^3 developed lacrimation, visual disturbances, and, in some cases, frontal headache, conjunctivitis, and cough. Application of a drop of 1% solution of osmium tetroxide to a rabbit eye caused severe corneal damage; there was permanent opacity and superficial vascularization. Osmium compounds have a caustic action on the skin resulting in eczema and dermatitis. Osmium tetroxide is a very irritating material to the skin due to its ability to precipitate protein.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 2.54
2. Boiling point (760 mm Hg): 130 C (266 F) (sublimes well below boiling point)
3. Specific gravity (water = 1): 4.9
4. Vapor density (air = 1 at boiling point of osmium tetroxide): 8.8
5. Melting point: 42 C (108 F)
6. Vapor pressure at 20 C (68 F): 7 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 7
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with hydrochloric acid will cause formation of poisonous chlorine gas. Contact with easily oxidized organic materials may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: According to Hunter, osmium tetroxide has an irritating odor, but no quantitative information is available concerning the odor threshold.

2. Eye Irritation Level: Grant states that "the eyes are particularly susceptible to injury by vapors of osmium tetroxide. With sufficient concentrations a sensation of irritation with lacrimation and sensation of foreign body is induced immediately. This may be accompanied by irritation of the nose and throat . . . . Concentrations of vapor which do not cause immediate sensation of irritation have an insidious cumulative action with a latent period before the onset of smarting and lacrimation, which may be delayed from 1 to several hours after start of exposure. In either case the symptoms and signs are those of keratitis epithelialis with corneal epithelial edema . . . . No permanent effect has been noted, even when several episodes of keratitis epithelialis have been experienced." Grant later states, however, that application of a drop of 1% solution of osmium tetroxide on rabbit eyes resulted in "moderate permanent opacity."

3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of osmium tetroxide, and since this is such an extremely toxic substance, it should be treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for osmium tetroxide had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with osmium tetroxide or liquids containing osmium tetroxide, where skin contact may occur.
- If employees' clothing may have become contaminated with solid osmium tetroxide, employees should

change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with osmium tetroxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of osmium tetroxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the osmium tetroxide, the person performing the operation should be informed of osmium tetroxide's hazardous properties.
- Non-impervious clothing which becomes contaminated with osmium tetroxide should be removed promptly and not reworn until the osmium tetroxide is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid osmium tetroxide or liquids containing osmium tetroxide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid osmium tetroxide or liquids containing osmium tetroxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with osmium tetroxide should be promptly washed or showered to remove any osmium tetroxide.
- Eating and smoking should not be permitted in areas where solid or liquid osmium tetroxide or liquids containing osmium tetroxide are handled, processed, or stored.
- Employees who handle solid or liquid osmium tetroxide or liquids containing osmium tetroxide should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to osmium tetroxide may occur and control methods which may be effective in each case:

Operation	Controls
By-product during refining and processing of osmiridium and other platinum metal ores; during production of alloys; during casting and annealing operations in manufacture of specialty metal products	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an intermediate for separation of metals and ores of osmium from platinum; use as a catalyst for oxidizing agent in organic synthesis; use as a staining and fixing agent in pathological and histological analysis; use as a laboratory reagent	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If osmium tetroxide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid osmium tetroxide or liquids containing osmium tetroxide get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solid or liquid osmium tetroxide or liquids containing osmium tetroxide penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of osmium tetroxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When osmium tetroxide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If solid or liquid osmium tetroxide or liquids containing osmium tetroxide are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing osmium tetroxide should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Osmium tetroxide may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Osmium Tetroxide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR OSMIUM TETROXIDE

Condition	Minimum Respiratory Protection* Required Above 0.002 mg/m^3
Particulate and Vapor Concentration	
0.1 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a high efficiency filter providing protection against osmium tetroxide vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Oxalic Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HOOCCOOH\text{-}2H_2O$
- Synonyms: Oxalic acid dihydrate; ethanedioic acid
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for oxalic acid is 1 milligram of oxalic acid per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Oxalic acid can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may slowly enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to either solid or liquid oxalic acid can cause severe burns of the skin, eyes, and linings of the respiratory tract. A number of deaths have occurred from swallowing oxalic acid. The symptoms appear rapidly and include shock, collapse, and convulsive seizures. Such cases may also have marked kidney damage.

2. Long-term Exposure: Prolonged or repeated skin contact with oxalic acid solutions may cause pain and discoloration of the fingers. This may go on to gangrene.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to oxalic acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to oxalic acid at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from oxalic acid exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of oxalic acid might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Oxalic acid is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Oxalic acid may cause kidney damage. Special consideration should be given to exposing those with impaired renal function.

—Eye disease: Oxalic acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Oxalic acid as a dust or in solution irritates the eyes, mucous membranes, and skin. There is little reported information on industrial exposures, although chronic inflammation of the upper respiratory tract has been described in a worker exposed to hot vapors (probably an aerosol) arising from oxalic acid. Solutions are irritating to the skin after prolonged exposure and may cause localized pain, with cyanosis of the fingers and even gangrenous changes. Splashes in the eye produce epithelial damage from which recovery is usually prompt. Fatalities have been reported following ingestion of as little as 5 g; the onset of symptoms is rapid, including those of shock, collapse, and convulsions;

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there may be marked renal damage, with deposition of calcium oxalate in the lumen of the renal tubules.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 126.1
2. Boiling point (760 mm Hg): Sublimes at 149 – 160 C (300 – 320 F) with partial decomposition
3. Specific gravity (water = 1): 1.5
4. Vapor density (air = 1 at boiling point of oxalic acid): 4.3
5. Melting point: 101.5 C (215 F)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 10
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with silver compounds may form explosive silver oxalate salt.
3. Hazardous decomposition products: Toxic gases and vapors (such as formic acid and carbon monoxide) may be released in a fire involving oxalic acid.
4. Special precautions: None

- **Flammability**

1. Flash point: None by standard tests
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Water spray, dry chemical, or carbon dioxide

- **Warning properties**

Grant reports that "oxalic acid, a crystalline solid, readily soluble in water, has caused burns of the human eye in a few instances when solutions accidentally came in contact with the eye. The injury has been epithelial, and recovery has been prompt, the epithelium regenerating usually within two days . . . ." Grant observed that the application of a 5% solution for 30 seconds to rabbit eyes caused "coagulation of the epithelium, but the cornea recovered within six days." Since oxalic acid is readily soluble in water, the dust and mists of solutions of this material are treated as eye irritants for the purposes of this guideline. No quantitative information is available concerning the concentrations which produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for oxalic acid had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with oxalic acid or liquids containing oxalic acid.
- If employees' clothing may have become contaminated with oxalic acid or liquids containing oxalic acid, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with oxalic acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of oxalic acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the oxalic acid, the person performing the operation should be informed of oxalic acid's hazardous properties.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of oxalic acid or liquids containing oxalic acid contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to oxalic acid or liquids containing oxalic acid, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with oxalic acid should be promptly washed or showered to remove any oxalic acid.
- Eating and smoking should not be permitted in areas where oxalic acid or liquids containing oxalic acid are handled, processed, or stored.
- Employees who handle oxalic acid or liquids containing oxalic acid should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to oxalic acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in metal cleaning and polishing operations for automobile radiators, boilers, and railroad cars to remove carbonaceous deposits from steel	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in textile cleaning and bleaching operations for rust, ink, and stain; bleaching of cotton and other fabrics; removal of discoloration from bleeding dyes; use as a sour in treatment of woolen and other piece goods; use in stripping and finishing operations in textile manufacture	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in bleaching and tanning of hides in leather manufacture	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during miscellaneous bleaching operations of wood, rosin, and cork	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of household and industrial cleaning and bleaching agents for metal and wood cleaning, cleaning preparations, disinfectants, and wax and grease removal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metallurgical processing of tin and extraction and purification of rare earth and actinide metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in synthesis of other chemicals for manufacture of dyes, blue-print photography, and acids and starch hydrolysis	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in extraction and purification operations for chemicals, natural gums, and tall oil	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in lithography and photoengraving operations; use as an analytical reagent; use in manufacture of inks and lacquers; and in synthesis of pharmaceuticals	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If oxalic acid or liquids containing oxalic acid get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If oxalic acid or liquids containing oxalic acid get on the skin, promptly flush the contaminated skin with water. If oxalic acid or liquids containing oxalic acid penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of oxalic acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When oxalic acid or liquids containing oxalic acid have been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the oxalic acid. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If oxalic acid is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Oxalic acid may be disposed of:

1. By making packages of oxalic acid in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving oxalic acid in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR OXALIC ACID

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Oxygen Difluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: OF_2
- Synonyms: Difluorine monoxide; fluorine monoxide
- Appearance and odor: Colorless gas with a foul odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for oxygen difluoride is 0.05 part of oxygen difluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.1 milligram of oxygen difluoride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Oxygen difluoride can affect the body if it is inhaled or if strong concentrations of oxygen difluoride gas contact the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of oxygen difluoride has produced severe headaches in humans. Although there are no reports regarding the effects of exposure to this chemical on the eyes or skin of humans, it would be expected that contact of the gas under pressure with the eyes or skin would cause burns. In animal experiments, inhalation of oxygen difluoride has caused tearing, shortness of breath, muscular weakness, vomiting, severe breathing difficulties (which are sometimes delayed in onset), and death.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to oxygen difluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to oxygen difluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs and eyes should be stressed.

—14" x 17" chest roentgenogram: Oxygen difluoride causes lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Oxygen difluoride is a severe pulmonary irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Oxygen difluoride gas is a severe respiratory irritant. In monkeys and dogs, the LC50 was 26 ppm for 60 minutes; signs of toxicity were lacrimation, dyspnea, muscular weakness, and vomiting; at autopsy, massive pulmonary edema and hemorrhage were observed. In mice, exposure to a low concentration (1 ppm for 60 minutes) produced tolerance to subsequent exposures 8 days later at levels which would otherwise have been fatal (4.25 ppm for 60 minutes). In humans, inhalation of the gas at fractions of a ppm produced intractable headache. Although there are no reports of effects on the eyes or skin of humans, it would be expected that

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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the gas under pressure impinging upon the eyes or skin would produce serious burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 54
2. Boiling point (760 mm Hg): −145 C (−229 F)
3. Specific gravity (water = 1): 1.5 (liquid at boiling point)
4. Vapor density (air = 1 at boiling point of oxygen difluoride): 1.86
5. Melting point: −224 C (−371 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.02 (reacts slowly)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures greater than 250 C (482 F) will cause oxygen difluoride to decompose and cause pressure increases in cylinders.
2. Incompatibilities: Contact with all combustible materials, chlorine, bromine, iodine, platinum, and many other metals, metal oxides, and moist air may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and carbon monoxide) may be released when oxygen difluoride decomposes.
4. Special precautions: Oxygen difluoride will attack some forms of plastics, rubber, and coatings. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Flammability**

1. Not combustible, but strong oxidizing agent

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of oxygen difluoride can be detected by some persons at 0.1 ppm and by most at 0.5 ppm. The odor, however, may not be relied upon for warning purposes, as it is not characteristic and because olfactory fatigue develops rapidly."
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "no signs of irritation of the external mucosa of the eye were observed in rats subjected to the lethal exposure of 15 ppm oxygen difluoride for 15 minutes."
3. Evaluation of Warning Properties: Since the *Hygienic Guide* points out that "olfactory fatigue develops rapidly" upon exposure to oxygen difluoride, and since no other quantitative information is available relating its warning properties to air concentrations, this gas is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for oxygen difluoride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to oxygen difluoride may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use as an oxidizer in rocket propellants	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If strong concentrations of oxygen difluoride gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately.

- **Skin Exposure**

If strong concentrations of oxygen difluoride gas get on the skin, immediately wash the skin with large quantities of water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of oxygen difluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If oxygen difluoride is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty with a mixed solution of caustic soda and slaked lime.

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- American Conference of Governmental Industrial Hygienists: "Oxygen Difluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR OXYGEN DIFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Gas Concentration	
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 0.5 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against oxygen difluoride.*** Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of oxygen difluoride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 0.5 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

***Oxygen difluoride is an strong oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore should not be used to provide protection against oxygen difluoride. Only non-oxidizable sorbents should be used.

Occupational Health Guideline for Ozone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: O_3
- Synonyms: None
- Appearance and odor: Colorless gas with a sharp, characteristic odor; it can be smelled at concentrations below the permissible exposure level.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ozone is 0.1 part of ozone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of ozone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ozone affects the body by being inhaled or by irritating the eyes, nose, and throat.

- **Effects of overexposure**

When a person is exposed to very low concentrations of ozone for even a brief period of time, the person may notice a sharp, irritating odor. As the concentration of ozone increases, the ability to smell it may decrease. Irritation of the eyes, dryness of the nose and throat, and cough may be experienced. If the ozone concentration continues to rise, more severe symptoms may develop. These may include headache, upset stomach, or vomiting, pain or tightness in the chest, shortness of breath or tiredness, which may last for several days to weeks. Finally, with higher levels of exposure, the lungs may be damaged and death may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ozone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ozone at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the heart and lungs should be stressed.

—14" x 17" chest roentgenogram: Ozone may cause lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ozone is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Ozone is extremely irritating to the upper and lower respiratory tract. The characteristic odor is readily detectable at low concentrations (0.01 ppm to 0.05 ppm). Ozone produces local irritation of the eyes and mucous membranes and may cause pulmonary edema at high exposure. Systemically, ozone has been reported to mimic the effects of ionizing radiation, and may cause damage to chromosomal structures. A partial tolerance appears to develop with repeated exposures. Although most effects are acute, the possibility of chronic lung impairment should be considered, based upon animal experimentation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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1. Molecular weight: 48
2. Boiling point (760 mm Hg): −112 C (−169.6 F)
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of ozone): 1.65
5. Melting point: −192 C (−313 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00003 (3 ppm)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Ozone spontaneously decomposes under all ordinary conditions, so that it is not encountered except in the immediate vicinity of where it was formed. The decomposition is speeded by solid surfaces and by many chemical substances.
2. Incompatibilities: Ozone is a powerful oxidizing agent and reacts with all oxidizable materials, both organic and inorganic. Some reaction products are highly explosive.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Use large amounts of water spray.

- **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold for ozone of 0.1 ppm.
2. Irritation Levels: Grant reports that "at concentrations greater than 1 ppm in air, ozone has been found irritating to the eyes and nose and injurious to the respiratory tract. Concentrations of 2 to 3.7 ppm caused sensation of irritation to normal human eyes within 6 minutes."
3. Evaluation of Warning Properties: Since the odor threshold of ozone is at the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of ozone in an impinger containing potassium iodide in sodium hydroxide, followed by treatment with phosphoric-sulfamic acid reagent, and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ozone may be used. An analytical method for ozone is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ozone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during welding operations with inert gas-shielded arc welding devices	Local exhaust ventilation; canister respirator; shielding (to block rays)
Liberation during welding operations with argon-shielded, bare-wire arc welding (especially stainless steel, aluminum, and aluminum alloy containing silicon)	Large-volume local exhaust; general dilution ventilation; direct fresh air supply; shielding (to block rays)
Liberation during arc welding operations in confined spaces	Direct fresh air supply
Liberation during production of ozone	Process enclosure; local exhaust ventilation

Operation	Controls
Liberation during oxidizing process of fine organic chemicals production (primarily ozolaic acid)	Process enclosure; local exhaust ventilation
Liberation during operations involving high-intensity ultraviolet light (plasma torch operations, glass blowing, hot metal operations, photoengraving operations, and use of mercury vapor lamps, direct copying machines, and projecting equipment)	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during operations involving high-voltage electrical equipment (spectrographic and fluorometric apparatus, electroplating operations, high-volt linear accelerators, and electrostatic precipitators)	Local exhaust ventilation
Liberation during operations involving ozonizing process in treatment of water, industrial waste, and sewage; during air purification	Local exhaust ventilation; process enclosure; respiratory protective equipment
Liberation during drilling, cutting, and welding operations utilizing laser radiation	Local exhaust or general dilution ventilation
Liberaton during bleaching operations (textiles, paper, pulp, waxes, starch, sugar, teflon, and synthetic fibers); during refining of mineral oils and their derivatives; during processing of perfumes, vanilin, amd camphor; during aging and drying operations (wood, wines, whiskies, varnishes, and printing inks)	Process enclosure; local exhaust ventilation
Liberation during food preserving operations for mold and bacteria control in food storage and deodorization	Exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ozone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible.

- **Breathing**

If a person breathes in large amounts of ozone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. When breathing is difficult, properly trained personnel may assist the affected person by administering 100% oxygen. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If ozone is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas.

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RESPIRATORY PROTECTION FOR OZONE

Condition	**Minimum Respiratory Protection* Required Above 0.1 ppm**
Vapor Concentration	
1 ppm or less	Any chemical cartridge respirator with a cartridge(s) containing non-oxidizable sorbents and providing protection against ozone. Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) containing non-oxidizable sorbents and providing protection against ozone. A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against ozone. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against ozone. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Paraquat

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: (a) $C_{12}H_{14}N_2Cl_2$; (b) $C_{12}H_{14}N_2(CH_3SO_4)_2$
- Synonyms: (a) 1,1'-dimethyl-4,4'-bipyridinium dichloride; (b) 1,1'-dimethyl-4,4'-bipyridinium bis (methosulfate)
- Appearance and odor: Odorless, colorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for paraquat is 0.5 milligram of paraquat per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for paraquat a Threshold Limit Value of 0.1 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Paraquat can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to paraquat may cause irritation of the eyes, nose, throat, and skin. It may also cause nose bleeding and abnormalities or loss of fingernails. Exposure to mixtures of paraquat and a related compound, diquat, may cause serious and permanent injury to the eyes. Swallowing paraquat may cause burning in the mouth and throat, nausea, vomiting, abdominal pain, diarrhea, heart, kidney, and lung damage, and liver damage with yellow jaundice.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to paraquat.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to paraquat at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory system, heart, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Paraquat causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Paraquat is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Urinalysis: Since kidney damage has been observed in humans exposed to paraquat, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to paraquat, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Paraquat as a mist or aerosol is an irritant of the eyes, mucous membranes, and skin. In rats exposed to aero-

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sols of paraquat, the LC50 for 6 hours was 1 mg/m@3@; death was delayed and resulted from pulmonary hemorrhage and edema. In a study of 30 workers spraying paraquat over a 12 week period, approximately 50% of them had minor irritation of the eyes or nose; 1 worker had an episode of epistaxis. Of 296 spray operators with skin exposure described as gross and prolonged, 55 had damaged fingernails; the most common lesion was transverse white bands of discoloration, but loss of nail surface, transverse ridging, gross deformity of the nail plate, and loss of nails also occurred. Paraquat is commonly combined in commercial herbicides with diquat, a related compound; in several instances the commercial preparations splashed in the eyes have caused serious injury. There have been loss of corneal and conjunctival epithelium, mild iritis, and residual corneal scarring. In contrast, in the eye of a rabbit, one drop of a 50% aqueous solution of pure paraquat caused slow development of mild conjunctival inflammation, and pure diquat proved even less irritating. Presumably the surfactants present in the commercial preparations are responsible for the severe eye injuries in humans. The results from injection or ingestion of paraquat are in marked contrast to the irritant effects usually encountered from occupational exposure. Intraperitoneal injection or oral administration to rats at doses which caused delayed death resulted in a peculiar proliferative lesion in the lung; there was alveolar, perivascular, and peribronchial edema, with cellular proliferation into the alveolar walls resulting in large solid areas of the lung with no air-containing cavities. There are several reports of fatal accidental ingestion by humans; in 2 cases, one person ingested about 114 ml of a 20% solution, while the other was believed to have taken only a mouthful of the liquid, most of which was rejected immediately; the former died after 7 days and the latter after 15 days. Initial symptoms included burning in the mouth and throat, nausea, vomiting, and abdominal pain with diarrhea. After 2 to 3 days, signs of liver and kidney toxicity developed including jaundice, oliguria, and albuminuria; there were E.C.G. changes suggesting toxic myocarditis with conduction defects. Shortly before death there was respiratory distress; at autopsy, findings in the lung included hemorrhage, edema, and massive solid areas which were airless owing to fibroblastic proliferation in the alveolar walls and elsewhere. There is no evidence that inhalation or skin absorption causes the rapid progressive pulmonary fibrosis and injury to the heart, liver, and kidneys occurring from ingestion.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: (a) 257.2; (b) 408
2. Boiling point (760 mm Hg): Decomposes at 175–180 C (347–356 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of paraquat): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, oxides of nitrogen and sulfur, and carbon monoxide) may be released when paraquat decomposes.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Grant states that "in tests on rabbit eyes pure paraquat at 50% concentration caused only mild superficial inflammation, developing in twelve hours and clearing in two to four days with no damage to the cornea."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for paraquat is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforce-

ment and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with paraquat or solutions containing paraquat, where skin contact may occur.
- Clothing contaminated with paraquat should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of paraquat from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the paraquat, the person performing the operation should be informed of paraquat's hazardous properties.
- Where exposure of an employee's body to paraquat or solutions containing paraquat may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with paraquat should be removed immediately and not reworn until the paraquat is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where paraquat or solutions containing paraquat may contact the eyes.

SANITATION

- Skin that becomes contaminated with paraquat should be immediately washed or showered to remove any paraquat.
- Eating and smoking should not be permitted in areas where paraquat or solutions containing paraquat are handled, processed, or stored.
- Employees who handle paraquat or solutions containing paraquat should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to paraquat may occur and control methods which may be effective in each case:

Operation	Controls
Use as an agricultural herbicide, desiccant, defoliation agent during pre-harvest; use as an herbicide for non-agricultural purposes on highway margins, around commercial buildings; use to control aquatic weeds	Personal protective equipment
Manufacture, formulation, and processing of paraquat and aqueous solutions of the salts	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If paraquat or solutions containing paraquat get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If paraquat or solutions containing paraquat get on the skin, immediately flush the contaminated skin with water. If paraquat or solutions containing paraquat soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of paraquat, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When paraquat or solutions containing paraquat have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If paraquat is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing paraquat should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Paraquat may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR PARAQUAT

Condition	**Minimum Respiratory Protection*** **Required Above 0.5 mg/m³**
Particulate Concentration	
1.5 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 1.5 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of paraquat; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 1.5 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Parathion

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5O)_2 PSOC_6H_4NO_2$
- Synonyms: O,O-Diethyl-O,p-nitrophenyl phosphorothioate; ethyl parathion
- Appearance and odor: Yellow to dark brown liquid with a characteristic odor, like garlic.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for parathion is 0.1 milligram of parathion per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 0.05 mg/m^3. The NIOSH Criteria Document for Parathion should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Parathion can affect the body if it is inhaled, comes in contact with the eyes or skin, or if swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of parathion, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing parathion, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur, usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to the above symptoms, weakness, generalized twitching, and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heartbeat, convulsions and coma may occur.

2. Long-term Exposure: Repeated exposure to parathion may make a person more susceptible to the effects of this and related chemicals. Repeated exposure to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to parathion.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to parathion at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, eyes, and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Cholinesterase determination: Parathion causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using

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medically acceptable biochemical tests prior to any new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination. This test should be performed at four-week intervals, except for those employees in areas which may involve intense exposure, for whom the test should be repeated weekly. If any employee works with parathion more than 12 hours per day, he should be tested every 3 weeks. Employees should also be tested at any time overexposure is suspected or signs or symptoms of toxicity appear. Any employee having a 30 to 40% decrease in cholinesterase should be removed from exposure and placed under medical observation.

- **Summary of toxicology**

Parathion is an anticholinesterase agent; absorption may occur from inhalation of the vapor or mist, from skin absorption of the liquid, or from ingestion. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system and skeletal and smooth muscle secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms may occur promptly or may be delayed for up to 12 hours. After inhalation respiratory and ocular effects are the first to appear, , often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects, such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures, and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for weeks after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects. A few drops of technical parathion in the eyes of animals have produced lacrimation and moderate conjunctivitis. The minimum lethal oral dose of parathion for humans has been estimated to range from less than 10 mg up to 120 mg. In a study of 115 workers exposed to parathion under varying conditions, the majority excreted significant amounts of p-nitrophenol (a metabolite of parathion) in the urine, while only those with heavier exposures had a measurable decrease in blood cholinesterase.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 291.3
2. Boiling point (760 mm Hg): 375 C (707 F) (calculated)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of parathion): Not applicable
5. Melting point: 6 C (43 F) (pure grade); 0 C (32 F) (technical grade)
6. Vapor pressure at 20 C (68 F): 0.0004 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): .00002
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 100 C (212 F) may cause decomposition so that containers burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, phosphorus, sulfur, and carbon monoxide) may be released when parathion decomposes.
4. Special precautions: Parathion will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The odor threshold of parathion is 0.04 ppm (American Society of Testing Materials Bulletin).
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "a few drops of technical parathion in animals has produced immediate blinking, lacrimation, and moderate conjunctivitis. Pupil constriction was also observed, with a return to normal size and reaction the following day. Eye contact with 1% aqueous suspensions of 15% wettable powders did not show evidence of irritation or other obvious reaction."
3. Evaluation of Warning Properties: Since the odor threshold of parathion is so low, parathion is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of parathion using a filter with subsequent recovery with iso-octane and gas chromatographic analysis. A detailed analytical method for parathion may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set T" (order number PB 262 404).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with parathion.
- If employees' clothing has had any possibility of being contaminated with parathion, employees should change into uncontaminated clothing before leaving the work premises.
- Where there is any possibility of exposure of an employee's body to parathion, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with parathion should be removed immediately and not reworn until the parathion is removed from the clothing.
- Clothing which has had any possibility of being contaminated with parathion should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of parathion from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the parathion, the person performing the operation should be informed of parathion's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid parathion contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to parathion, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with parathion should be immediately washed or showered with soap or mild detergent and water to remove any parathion.
- Workers subject to skin contact with parathion should wash with soap or mild detergent and water any areas of the body which may have contacted parathion at the end of each work day.
- Eating and smoking should not be permitted in areas where parathion is handled, processed, or stored.
- Employees who handle parathion should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to parathion may occur and control methods which may be effective in each case:

Operation	Controls
Application as a pesticide on agricultural crops, vegetables and ornamentals and on agricultural premises	Personal protective equipment
Formulation for use as an insecticide	Process enclosure; personal protective equipment
Manufacture of parathion	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If parathion or parathion mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If parathion or parathion mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If parathion or parathion mists penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of parathion, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When parathion has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If parathion is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation, or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Parathion may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR PARATHION

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m^3**
Particulate or Vapor Concentration	
1 mg/m^3 or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust, fume, and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m^3 or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20 mg/m^3** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of parathion; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Pentaborane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: B_5H_9
- Synonyms: Stable pentaborane, pentaboron anhydride
- Appearance and odor: Colorless liquid with a strong, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentaborane is 0.005 part of pentaborane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.01 milligram of pentaborane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentaborane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to low concentrations of pentaborane may cause lightheadedness, drowsiness, nervousness, lack of coordination, and tremors. The onset of these symptoms may be delayed as long as 48 hours. After exposure to higher concentrations, the onset of symptoms may be prompt and may include the above symptoms plus spasms of the face, neck, arms, legs, and abdomen. After severe exposure, convulsions may occur. In animals impairment of liver and kidney function has been reported. Also, in animals, the vapor has caused severe irritation of the eyes and the liquid has caused inflammation of the skin.

2. Long-term Exposure: Prolonged exposure to low concentrations of pentaborane may cause headache, fatigue, drowsiness, the inability to concentrate, and the lack of coordination.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to pentaborane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentaborane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders would be expected to be at increased risk from exposure. Examination of the nervous system, liver, and kidneys should be stressed. The skin and eyes should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Pentaborane vapor affects the nervous system and causes signs of both hyperexcitability and narcosis. Exposure of rats to 10 ppm for 2 hours was fatal; effects included weakness, incoordination, corneal opacities, tremors, and convulsions; other animal studies have indicated that kidney and liver damage may occur. In humans, the onset of symptoms may be delayed up to 48 hours after exposure; dizziness, headache, and drowsiness are common; other symptoms include fatigue, incoordination, and tremor. After exposure to higher concentrations, the onset of symptoms may be prompt and include tonic spasms of the muscles of the face,

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neck, abdomen, and extremities; after severe exposures, convulsive seizures may occur. The results of exposure to animals for 60 minutes are: 8 ppm, some decrement in performance of learned tasks and slight signs of toxicity; 15 ppm, convulsions; 30 ppm, convulsions and death. Severe irritation and corneal opacity of the eyes of test animals occurred from exposure to the vapor; the liquid on the skin of animals caused acute inflammation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 63.1
2. Boiling point (760 mm Hg): 58.4 C (137 F)
3. Specific gravity (water = 1): 0.63
4. Vapor density (air = 1 at boiling point of pentaborane): 2.2
5. Melting point: −47 C (−52 F)
6. Vapor pressure at 20 C (68 F): 171 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts slowly to form hydrogen gas
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 150 C (302 F) cause decomposition and pressure buildup in containers.
2. Incompatibilities: Pentaborane reacts with oxidizers to form highly explosive mixtures. Contact with halogens or halogenated compounds may cause explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as boron acids) may be released in a fire involving pentaborane.
4. Special precautions: Pentaborane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 30 C (86 F) (closed cup when pure); impure material ignites spontaneously in air
2. Autoignition temperature: 35 C (95 F) (impure material ignites at lower temperatures)
3. Flammable limits in air, % by volume: Lower: 0.42; Upper: Not obtainable
4. Extinguishant: Let small fires burn. Water spray, foam, dry chemical, and carbon dioxide will decrease intensity of large fires. Do not use halogenated extinguishing fluids.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that pentaborane has a characteristic odor, but that it is "not a reliable index of exposure." According to a technical bulletin from Callery Chemical Company, the median detectable concentration of pentaborane by odor is 2.5 mg/m@3@, which is many times greater than the permissible exposure limit.
2. Eye Irritation Level: Pentaborane vapor is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold is many times greater than the permissible exposure limit of pentaborane, and since there is no other quantitative information relating warning properties to air concentrations of pentaborane, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for pentaborane had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid pentaborane, where skin contact may occur.
- Clothing wet with liquid pentaborane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentaborane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentaborane, the person performing the operation should be informed of pentaborane's hazardous properties.

- Where exposure of an employee's body to liquid pentaborane may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with liquid pentaborane should be removed immediately and not reworn until the pentaborane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid pentaborane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid pentaborane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid pentaborane should be immediately washed or showered with soap or mild detergent and water to remove any pentaborane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pentaborane may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical research as jet and rocket fuels, catalysts, corrosion inhibitor-fluxing agents, and oxygen scavengers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a chemical intermediate (higher boranes, alkyl boranes— ethyl pentaborane and various hydrides); these are not industrial chemicals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid pentaborane or strong concentrations of pentaborane vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention promptly. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid pentaborane or strong concentrations of pentaborane vapor get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid pentaborane or strong concentrations of pentaborane vapor penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of pentaborane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid pentaborane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If pentaborane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Pentaborane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of pentaborane vapors are permitted.

- Waste disposal method:

Pentaborane may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR PENTABORANE

Condition	**Minimum Respiratory Protection* Required Above 0.005 ppm**
Vapor Concentration	
0.05 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
0.25 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 3 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against pentaborane. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Pentachloronaphthalene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_3Cl_5$
- Synonyms: Halowax 1013
- Appearance and odor: Pale, yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentachloronaphthalene is 0.5 milligram of pentachloronaphthalene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentachloronaphthalene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Overexposure to pentachloronaphthalene causes headache and dizziness. Prolonged overexposure to pentachloronaphthalene may cause an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, yellow jaundice, and possibly death.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to pentachloronaphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentachloronaphthalene at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Pentachloronaphthalene may cause liver damage. A profile of liver function should be performed by using a medically acceptable array of biochemical tests.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Pentachloronaphthalene is a severe hepatic toxin, with marked effects upon the skin. While a solid at room temperature, the heated liquid produces a hazardous vapor. Rats exposed to the vapor of a mixture of hexa- and pentachloronaphthalene at average concentrations of 1.16 mg/m^3 for 16 hours daily up to 4-½ months showed definite liver injury, while 8.8 mg/m^3 produced some mortality and severe liver injury. The most striking human response to prolonged skin contact with the solid, or to shorter term inhalation of hot vapors, is chloracne. This is an acne-form skin eruption characterized by papules, large comedones and pustules, chiefly affecting the face, neck, arms, and legs. Pruritic erythematous and vasculoerythematous reactions have also been reported. Skin lesions are often accompanied by symptoms of systemic effects, including headache, vertigo, and anorexia. Liver damage characterized by toxic jaundice, which may progress to fatal hepatic necrosis, results from the inhalation of higher concentrations of the hot fumes of the molten substance. Skin absorption

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has been demonstrated in animals and is suspected in man.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 300.5
2. Boiling point (760 mm Hg): 327 to 371 C (620 to 700 F)
3. Specific gravity (water = 1): 1.67
4. Vapor density (air = 1 at boiling point of pentachloronaphthalene): 10.4
5. Melting point: 120 C (248 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and toxic chloride fumes) may be released in a fire involving pentachloronaphthalene.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "eye injury has not proved to be troublesome with the chloronaphthalenes;" nonetheless, they specifically state that "if respirators are used, they should be of the full-facepiece type approved by the U. S. Bureau of Mines for disperoids or organic vapors."
3. Evaluation of Warning Properties: There are no quantitative data relating warning properties to air concentrations of pentachloronaphthalene; therefore, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of pentachloronaphthalene with a filter and a bubbler containing iso-octane, followed by gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure pentachloronaphthalene may be used. An analytical method for pentachloronaphthalene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten pentachloronaphthalene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid pentachloronaphthalene or liquids containing pentachloronaphthalene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with pentachloronaphthalene vapors from the heated material.
- If employees' clothing may have become contaminated with solid pentachloronaphthalene, employees

should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with pentachloronaphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentachloronaphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentachloronaphthalene, the person performing the operation should be informed of pentachloronaphthalene's hazardous properties.
- Non-impervious clothing which becomes contaminated with molten pentachloronaphthalene should be removed immediately and not reworn until the pentachloronaphthalene is removed from the clothing.
- Non-impervious clothing which becomes contaminated with solid pentachloronaphthalene or liquids containing pentachloronaphthalene should be removed promptly and not reworn until the pentachloronaphthalene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten pentachloronaphthalene contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where solid pentachloronaphthalene or liquids containing pentachloronaphthalene may contact the eyes.

SANITATION

- Workers subject to skin contact with pentachloronaphthalene should wash with soap or mild detergent and water any areas of the body which may have contacted pentachloronaphthalene at the end of each work day.
- Skin that becomes contaminated with pentachloronaphthalene should be promptly washed or showered with soap or mild detergent and water to remove any pentachloronaphthalene.
- Eating and smoking should not be permitted in areas where solid pentachloronaphthalene is handled, processed, or stored.
- Employees who handle solid pentachloronaphthalene or liquids containing pentachloronaphthalene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pentachloronaphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture of electric equipment as an insulating material; pouring molten solvent or finely ground solid materials; dipping; peeling and covering insulated cable with fabric	Local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Liberation from use of electrical equipment insulated with octachloronaphthalene/pentachloronaphthalene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an inert compound of resins or polymers for coating or impregnating textiles, wood, and paper to impart flame resistance, water proofness, and fungicidal and insecticidal properties	Process enclosure; local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Use as an additive for cutting oil in various operations performed on metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive to special lubricants in crankcase oil, lubricants for farm machinery, and extreme-pressure lubricants	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid pentachloronaphthalene or liquids containing pentachloronaphthalene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. If molten pentachloronaphthalene gets into the eyes, immediately flush the eyes with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If non-impervious clothing becomes contaminated with pentachloronaphthalene, remove and clean the clothing before wearing again.If non-impervious clothing becomes heavily contaminated, it should be destroyed. If solid pentachloronaphthalene or liquids containing pentachloronaphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If irritation persists after washing, get medical attention. If molten pentachloronaphthalene gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of pentachloronaphthalene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When pentachloronaphthalene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If pentachloronaphthalene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing pentachloronaphthalene should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Pentachloronaphthalene may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Pentachloronaphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Chloronaphthalenes," *Hygienic Guide Series*, Detroit, Michigan, 1966.
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RESPIRATORY PROTECTION FOR PENTACHLORONAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
1000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Pentachlorophenol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6Cl_5OH
- Synonyms: PCP; penta
- Appearance and odor: Light brown solid with a pungent odor when hot.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentachlorophenol is 0.5 milligram of pentachlorophenol per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentachlorophenol can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to pentachlorophenol may cause irritation of the eyes and respiratory tract. Bronchitis has been reported to occur. Systemic effects from either a large exposure or repeated smaller exposures include weakness, loss of appetite, nausea, vomiting, shortness of breath, chest pain, excessive sweating, headache, and dizziness. In fatal cases the temperature is often very high and death may occur as early as three hours after the onset of symptoms. The risk of serious intoxication is greater in hot weather. Persons with decreased liver or kidney functions are more susceptible to poisoning from this chemical. Repeated exposure to pentachlorophenol may cause an acne-like skin rash and liver damage. Commercial pentachlorophenol may be contaminated with dioxin compounds which are much more toxic than pentachlorophenol.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to pentachlorophenol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentachlorophenol at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the cardiovascular system, eyes, upper respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders. Analysis of the urine for pentachlorophenol may be helpful in estimating the extent of absorption.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Pentachlorophenol dust and mist cause irritation of the eyes and upper respiratory tract; absorption results in an increase in metabolic rate and hyperpyrexia; prolonged skin exposure causes an acneform dermatitis. Human exposure to dust or mist concentrations greater than 1 mg/m^3 causes pain in the nose and throat, violent sneezing, and cough; 0.3 mg/m^3 may cause some nose irritation; persons acclimated to pentachlorophenol can tolerate concentrations up to 2.4 mg/m^3. Pentachlorophenol readily penetrates the skin; systemic intoxication is cumulative and has been fatal. Intoxication is characterized by weakness, anorexia, weight loss, and profuse sweating; there also may be headache, dizziness, nausea, vomiting, dyspnea, and chest pain. In fatal cases, the body temperature is frequently extremely high and

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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death has occurred as early as 3 hours after the onset of symptoms. The risk of serious intoxication is increased during hot weather; persons with impaired liver or kidney function are more susceptible to the effects of pentachlorophenol. The dust, mist, and vapor cause eye irritation. Prolonged exposure of workers has caused an acneform dermatitis; 10 workers engaged in production of pentachlorophenol for 5 to 10 months developed a widely disseminated skin eruption characterized by small and large furuncles, brown pigmentation, and some cicatrization; 7 workers also developed severe bronchitis; all but 1 worker still showed signs of extensive acne more than a year after cessation of exposure, and 4 still complained of bronchitis. On the skin, solutions of pentachlorophenol as dilute as 1% may cause irritation if contact is repeated or prolonged.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 266.3
2. Boiling point (760 mm Hg): 311 C (592 F) (decomposes)
3. Specific gravity (water = 1): 2.0
4. Vapor density (air = 1 at boiling point of pentachlorophenol): Not applicable
5. Melting point: 182 — 190 C (360 — 374 F)
6. Vapor pressure at 20 C (68 F): 0.00017 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.002
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorinated phenols, and carbon monoxide) may be released when pentachlorophenol decomposes.
4. Special precautions: None.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that pentachlorophenol has a characteristic odor. No quantitative information is available, however, concerning the odor threshold of this substance.
2. Irritation Levels: The *Documentation of TLV's* states that "dusts are particularly irritating to the eyes and nose, in concentrations appreciably greater than 1 mg/m^3, but some irritation of the nose may occur at 0.3 mg/m^3. Hardened workers can tolerate up to 2.4 mg/m^3."
3. Evaluation of Warning Properties: Through its irritant effects, pentachlorophenol can be detected within three times of the permissible exposure limit. For the purposes of this guideline, therefore, pentachlorophenol is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for pentachlorophenol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with pentachlorophenol or liquids containing pentachlorophenol.
- If employees' clothing has had any possibility of being contaminated with pentachlorophenol or liquids containing pentachlorophenol, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing which has had any possibility of being contaminated with pentachlorophenol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentachlorophenol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentachlorophenol, the person performing the operation should be informed of pentachlorophenol's hazardous properties.
- Where there is any possibility of exposure of an employee's body to pentachlorophenol or liquids containing pentachlorophenol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with pentachlorophenol should be removed immediately and not reworn until the pentachlorophenol is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of pentachlorophenol or liquids containing pentachlorophenol contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to pentachlorophenol or liquids containing pentachlorophenol, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with pentachlorophenol should be immediately washed or showered with soap or mild detergent and water to remove any pentachlorophenol.
- Workers subject to skin contact with pentachlorophenol or liquids containing pentachlorophenol should wash with soap or mild detergent and water any areas of the body which may have contacted pentachlorophenol at the end of each work day.
- Eating and smoking should not be permitted in areas where pentachlorophenol or liquids containing pentachlorophenol are handled, processed, or stored.
- Employees who handle pentachlorophenol or liquids containing pentachlorophenol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pentachlorophenol may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of preservatives, pesticides, and fungicides	Process enclosure; local exhaust ventilation; personal protective equipment
Application as a preservative for wood, starch, paint, adhesives, leather, latex, and oils; use in slime-algae control; use as a pesticide, herbicide, and snail control agent	Personal protective equipment
Manufacture of pentachlorophenol	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If pentachlorophenol or liquids containing pentachlorophenol get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If pentachlorophenol or liquids containing pentachlorophenol get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If pentachlorophenol or liquids containing pentachlorophenol penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of pentachlorophenol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When pentachlorophenol or liquids containing pentachlorophenol have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If pentachlorophenol is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and depost in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing pentachlorophenol should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Pentachlorophenol may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Pentachlorophenol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.
- Thienes, C. H., and Haley, T. J.: *Clinical Toxicology* (5th ed.), Lea and Febiger, Philadelphia, 1972.

RESPIRATORY PROTECTION FOR PENTACHLOROPHENOL

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
2.5 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m³ or less	Any chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust, fume, and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
150 mg/m³ or less	

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Pentane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_5H_{12}
- Synonyms: Normal pentane
- Appearance and odor: Colorless liquid with a gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentane is 1000 parts of pentane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2950 milligrams of pentane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 120 ppm (350 mg/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 610 ppm (1,800 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to pentane may cause drowsiness and irritation of the eyes and nose. Greater exposure may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to pentane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Pentane is a skin defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although pentane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although pentane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of pentane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: The aforementioned examinations should be performed on an annual basis.

- **Summary of toxicology**

Pentane vapor is a mild narcotic and mucous membrane irritant. Exposure to 90,000 to 120,000 ppm resulted in narcosis in animals in 5 to 6 minutes; 130,000 ppm was fatal, with respiratory arrest occurring within 5 minutes of the start of exposure. Pentane injected subcutaneous-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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ly in rats produced temporary impairment of liver function and moderate neutropenia. While other aliphatic hydrocarbons produce drowsiness and mild irritation of the eyes and nose in human subjects, no symptoms resulted from exposure to pentane vapor for 10 minutes at 5000 ppm. Repeated or prolonged skin contact results in drying and cracking due to defatting action. No chronic systemic effects have been reported in humans. Aspiration may cause chemical pneumonia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 72.2
  2. Boiling point (760 mm Hg): 36 C (97 F)
  3. Specific gravity (water = 1): 0.63
  4. Vapor density (air = 1 at boiling point of pentane): 2.5
  5. Melting point: −129 C (−200 F)
  6. Vapor pressure at 20 C (68 F): 426 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.04
  8. Evaporation rate (butyl acetate = 1): 28.6
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving pentane.
  4. Special precautions: Pentane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −49 C (−57 F) (closed cup)
  2. Autoignition temperature: 260 C (500 F)
  3. Flammable limits in air, % by volume: Lower: 1.5; Upper: 7.8
  4. Extinguishant: Foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: May reports an odor threshold of 2.2 ppm. The *Hygienic Guide* states that "the odor threshold of pentane vapor is approximately the same as the recommended maximal concentration of 1000 ppm."
  2. Eye Irritation Level: Pentane is not a known eye irritant.
  3. Evaluation of Warning Properties: Since its odor threshold is at or below the permissible exposure limit, pentane is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of pentane. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of pentane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure pentane may be used. An analytical method for pentane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid pentane.

- Any clothing which becomes wet with liquid pentane should be removed immediately and not reworn until the pentane is removed from the clothing.
- Clothing wet with liquid pentane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentane, the person performing the operation should be informed of pentane's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid pentane may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to pentane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid pentane should be promptly washed or showered with soap or mild detergent and water to remove any pentane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pentane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a gasoline additive for automotive, aviation, and farm equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in synthesis of amyl chlorides for intermediates in manufacture of paint and lacquer solvents, tube oil additives, hydraulic fluids, pesticides, paint removers, solvent extenders, and miscellaneous petrochemicals; use in synthesis of polychlorocyclopentanes as intermediates in manufacture of fire-resistant polyester resins and paints, dye intermediates, insecticides, and plasticizers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a blowing agent for polymeric foams	Local exhaust ventilation; general dilution ventilation
Use as a raw material in synthesis of olefins for synthetic rubber and other petrochemicals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in solvent extraction processes; use as a general laboratory solvent; use as a medium solvent for polymerization reactions	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a component of lighter fluids and blow-torch fuel	Local exhaust ventilation; general dilution ventilation
Use as a heat-exchange medium in manufacture of artificial ice; use in manufacture of low-temperature thermometers; use in manufacture of polystyrene beads for styrofoam production	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If pentane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If pentane gets on the skin, promptly wash the contaminated skin with water. If pentane soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of pentane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If pentane has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If pentane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Pentane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Pentane may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PENTANE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
5000 ppm or less	A gas mask with a chin-style or front- or back-mounted organic vapor canister. Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

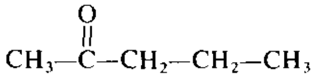
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-PENTANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-pentanone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_5H_{10}O$
- **Structure:**



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

- **Synonyms:** Ethyl acetone, methyl n-propyl ketone, MPK
- **Identifiers:** CAS 107-87-9; RTECS SA7875000; DOT 1249, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a powerful, ethereal, fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 86.15
2. Boiling point (at 760 mmHg): 102.3 °C (216 °F)
3. Specific gravity (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of 2-pentanone): 3.0
5. Melting point: -77.5 °C (-108 °F)
6. Vapor pressure at 25 °C (77 °F): 16 mmHg
7. Solubility in water, g/100 g water at 20 °C (68 °F): 4.3
8. Evaporation rate (butyl acetate = 1): 1.25
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 2.1% (21,000 ppm)
10. Ionization potential: 9.37 eV

- **Reactivity**

1. Incompatibilities: Oxidizing agents may cause fires and explosions
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving 2-pentanone
3. Caution: 2-Pentanone will dissolve some plastics, resins, and rubber.

- **Flammability**

1. Flash point: 7.2 °C (45 °F) (closed cup)
2. Autoignition temperature: 452 °C (846 °F)
3. Flammable limits in air, % by volume: Lower, 1.6; Upper, 8.2
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 11 ppm
2. Eye irritation levels: Humans exposed to 2-pentanone at 1,300 to 1,500 ppm found brief exposure severely irritating to the eyes, but no damage was produced.
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-pentanone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, 2-pentanone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-pentanone is 200 parts of 2-pentanone per million parts of air (ppm) [700 milligrams per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 150 ppm (530 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 200 ppm (700 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 250 ppm (875 mg/m^3) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for 2-pentanone

	Exposure limits ppm	Exposure limits mg/m³
OSHA PEL TWA	200	700
NIOSH REL TWA	150	530
ACGIH TLV® TWA	200	700
STEL	250	875

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Pentanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of 2-pentanone by guinea pigs caused narcosis and congestion, hemorrhage, and edema of the lungs, liver, and kidneys.
2. *Effects on humans:* Acute inhalation of 2-pentanone has caused narcosis and central nervous system depression.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 2-pentanone can cause headache, nausea, dizziness, vomiting, incoordination, and irritation of the eyes and respiratory passages.
2. *Long-term (chronic):* Dermal exposure to liquid 2-pentanone can cause dermatitis.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 2-pentanone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-pentanone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-pentanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to 2-pentanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting 2-pentanone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure 2-pentanone may also be used if available. A detailed sampling and analytical method for 2-pentanone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with 2-pentanone.

Workers should be provided with and required to use splash-proof safety goggles where 2-pentanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-pentanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-pentanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-pentanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with 2-pentanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-pentanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-pentanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 2-pentanone

Operations	Controls
During application of cellulose- or resin-based coatings, finishes, and adhesives	Local exhaust ventilation, general dilution ventilation
During oven or air drying of coatings, finishes, and adhesives; during use in the manufacture of pharmaceuticals and some flavorings; during use as an extractant in dewaxing petroleum products	General dilution ventilation
During blending of raw materials for molded plastics	Local exhaust ventilation, personal protective equipment
During cleaning and maintenance of ketone-processing equipment	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-pentanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-pentanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-pentanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-pentanone gets on the skin, wash it immediately with soap and water. If 2-pentanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 2-pentanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing 2-pentanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from 2-pentanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-pentanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Pentanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-pentanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors and meet other requirements of the decision logic may also be used.

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Table 3.—Respiratory protection for 2-petanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any powered air-purifying respirator with organic vapor cartridge(s)(substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1,500 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 3,750 ppm	Any supplied-air respirator operated in continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 5,000 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 5,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-equipment should be used.

†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 150 ppm (530 mg/m^3 (TWA).

Occupational Health Guideline for Perchloromethyl Mercaptan

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CCl_3SCl
- Synonyms: PMM; trichloromethylsulfur chloride; trichloromethanethiol; perchloromethanethiol
- Appearance and odor: Pale yellow, oily liquid with a foul-smelling, strong acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for perchloromethyl mercaptan is 0.1 part of perchloromethyl mercaptan per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.8 milligram of perchloromethyl mercaptan per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Perchloromethyl mercaptan can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Inhalation of perchloromethyl mercaptan vapor may cause irritation of the eyes, nose, throat, and lungs as well as nausea. An exposure to this chemical by inhalation and skin contact has caused severe breathing difficulty and death. Liver and kidney damage also occurred following this exposure. The liquid splashed on the skin or in the eyes will cause irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to perchloromethyl mercaptan.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to perchloromethyl mercaptan at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to perchloromethyl mercaptan, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—14" x 17" chest roentgenogram: Perchloromethyl mercaptan causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Perchloromethyl mercaptan is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Perchloromethyl mercaptan has been reported to cause liver damage in humans. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Perchloromethyl mercaptan vapor is a severe respiratory irritant and lacrimator. Mice and cats exposed for 15 minutes at 45 ppm died within 1 to 2 days from

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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pulmonary edema; 3-hour exposures at 9 ppm killed 50% of mice; repeated exposures over 3 months at 1 ppm resulted in the death of some mice. Eye irritation begins at 10 mg/m^3 (1.3 ppm). Exposure at higher concentrations causes marked irritation of the eyes, throat, and bronchi, as well as nausea. Three chemical workers were observed following accidental exposures to perchloromethyl mercaptan; two survived episodes of pulmonary edema, while the third died after 36 hours. The fatality resulted from a spill of the liquid on clothing and floor with exposure to the vapor. At autopsy, there was necrotizing tracheitis, massive hemorrhagic pulmonary edema, marked toxic nephrosis, and vacuolization of centrolobular hepatic cells. The liquid splashed on the skin may be expected to cause irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 185.9
2. Boiling point (760 mm Hg): 149 C (300 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of perchloromethyl mercaptan): 6.4
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 65 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble, reacts slowly to form hydrochloric acid, carbon dioxide, and sulfur.
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Perchloromethyl mercaptan decomposes at elevated temperatures to give carbon tetrachloride and sulfur monochloride. The decomposition is rapid at 149 C (300 F), the boiling point.
2. Incompatibilities: Contact with alkalies and amines may cause rapid decomposition. Contact with hot iron causes formation of toxic carbon tetrachloride vapor. Contact with hot water causes formation of hydrochloric acid, sulfur, and carbon dioxide.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon tetrachloride, sulfur monochloride, hydrogen chloride, sulfur dioxide, and carbon monoxide) may be released in a fire involving perchloromethyl mercaptan.
4. Special precautions: Perchloromethyl mercaptan will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: By analogy with other mercaptans, perchloromethyl mercaptan is assumed to have an odor threshold below the permissible exposure limit.

   In addition, the following odor thresholds for different mercaptans can be found in May: n-butyl mercaptan, 0.00082 ppm; i-butyl mercaptan, 0.00054 ppm; i-pentyl mercaptan, 0.00021 ppm; i-amyl mercaptan, 0.00043 ppm; allyl mercaptan, 0.00005 ppm; crotyl mercaptan, 0.00016 and 0.000056 ppm; benzyl mercaptan, 0.0026 and 0.00035 ppm.
2. Eye Irritation Level: Grant states that perchloromethyl mercaptan "is a stink and tear gas that has been of military interest." No quantitative information is available, however, concerning the levels which produce eye discomfort.
3. Other Information: Grant states that this substance is a respiratory tract irritant.
4. Evaluation of Warning Properties: Since the odor threshold of perchloromethyl mercaptan is considerably below the permissible exposure limit and odor may be present within a properly functioning respirator, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for perchloromethyl mercaptan had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid perchloromethyl mercaptan.
- Clothing wet with perchloromethyl mercaptan should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of perchloromethyl mercaptan from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the perchloromethyl mercaptan, the person performing the operation should be informed of perchloromethyl mercaptan's hazardous properties.
- Non-impervious clothing which becomes wet with liquid perchloromethyl mercaptan should be removed promptly and not reworn until the perchloromethyl mercaptan is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid perchloromethyl mercaptan may contact the eyes.

SANITATION

- Skin that becomes wet with liquid perchloromethyl mercaptan should be promptly washed or showered with soap or mild detergent and water to remove any perchloromethyl mercaptan.
- Employees who handle liquid perchloromethyl mercaptan should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to perchloromethyl mercaptan may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical synthesis for agricultural and dye chemicals; use as an organic intermediate	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid perchloromethyl mercaptan or strong concentrations of perchloromethyl mercaptan vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid perchloromethyl mercaptan gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid perchloromethyl mercaptan soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of perchloromethyl mercaptan, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid perchloromethyl mercaptan has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If perchloromethyl mercaptan is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal methods:

Perchloromethyl mercaptan may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By dissolving in a combustible solvent, such as alcohol, and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR PERCHLOROMETHYL MERCAPTAN

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Vapor Concentration	
1ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Perchloryl Fluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ClO_3F
- Synonyms: None
- Appearance and odor: Colorless gas with a characteristic sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for perchloryl fluoride is 3 parts of perchloryl fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 13.5 milligrams of perchloryl fluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Perchloryl fluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Perchloryl fluoride may cause respiratory irritation. The liquid, if allowed to remain in contact with the skin, may cause a burn. Animal exposures have produced severe breathing difficulties which have sometimes been delayed in onset. Also in animals, perchloryl fluoride can affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause a bluish discoloration of the skin, drowsiness, dizziness, rapid heart beat, nausea, headache, shortness of breath, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to perchloryl fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to perchloryl fluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory tract, blood, cardiovascular system, nervous system, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Perchloryl fluoride has been shown to cause methemoglobinemia in animals. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—14" x 17" chest roentgenogram: Perchloryl fluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Perchloryl fluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when other signs and symptoms of respiratory disease occur. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

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- **Summary of toxicology**

Perchloryl fluoride gas is a respiratory irritant in humans and in animals causes the formation of methemoglobin. Dogs exposed to 450 ppm or 620 ppm for 4 hours developed hyperpnea, cyanosis, incoordination, and convulsions; methemoglobin levels were 29% and 71%, respectively. In dogs which died from exposure, there was lung damage consisting of alveolar collapse and hemorrhage; pigment deposition in the liver, spleen, and bone marrow was observed. Repeated exposure of three species of animals to 185 ppm for 7 weeks caused the death of more than half of them, guinea pigs being the most susceptible; all of the animals developed dyspnea, cyanosis, methemoglobinemia, alveolar edema, and pneumonitis. With similar repeated exposure of animals to 104 ppm for 6 weeks, the fluoride levels were increased by a factor of 20 to 30 in the blood, 5 to 8 in the urine, and 12 in the rat femur. One report states that workers suffered symptoms of upper respiratory irritation from brief exposure to unspecified concentrations. Perchloryl fluoride has the potential to form methemoglobin in man; the effects of methemoglobinemia are due to anoxia and include cyanosis, evident especially in the lips, nose, and earlobes; other effects are weakness, dizziness, and severe headache. The liquid is reported to produce moderately severe burns with prolonged skin contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.5
2. Boiling point (760 mm Hg): −46.7 C (−52 F)
3. Specific gravity (water = 1): 1.41 (liquid at 25 C)
4. Vapor density (air = 1 at boiling point of perchloryl fluoride): 3.5
5. Melting point: −146 C (−231 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.06
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Containers may explode when heated above 500 C (932 F).
2. Incompatibilities: Contact with combustible materials, strong bases, amines, and finely divided metals may cause fires and explosions. Contact with readily oxidizable materials such as hydrogen sulfide, charcoal, sawdust, lampblack, etc. yields explosive products.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and chlorine) may be released when perchloryl fluoride decomposes.
4. Special precautions: Perchloryl fluoride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible by itself, but is a strong oxidizing agent
2. See 29 CFR 1910.101 for special regulations on storage of compressed gas cylinders.

- **Warning properties**

1. Odor Threshold: Sax states that the odor of perchloryl fluoride "can be detected as low as 10 ppm, although this cannot be relied upon as an indication of toxic concentrations in air."
2. Eye Irritation Level: Grant states that in industry "irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m³ of air." Perchloryl fluoride is not specifically known to be an eye irritant.
3. Evaluation of Warning Properties: Since Sax notes that the odor "cannot be relied upon as an indication of toxic concentrations in air," and since there is no other quantitative information relating warning properties to air concentrations of perchloryl fluoride, this substance is treated like a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for perchloryl fluoride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid perchloryl fluoride or vessels containing liquid perchloryl fluoride.
- Non-impervious clothing which becomes contaminated with liquid perchloryl fluoride should be removed immediately and not reworn until the perchloryl fluoride has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid perchloryl fluoride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to perchloryl fluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a liquid oxidizer in rocket fuels, fuels used in cutting and welding, torches and chemical machinery	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment
Use in chemical synthesis in oxidation, ammonolysis, fluorination, perchlorylation, and etherification	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment
Use in flame photometry for analysis of different elements; miscellaneous uses for manufacture of fuel cells, gaseous dielectric for transformers, explosives, and metal processing	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Skin Exposure**

If liquid perchloryl fluoride gets on the skin, immediately flush the perchloryl fluoride from the contaminated skin. If liquid perchloryl fluoride penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of perchloryl fluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If perchloryl fluoride is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR PERCHLORYL FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Vapor Concentration	
30 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
150 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
400 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode and containing non-combustible sorbents.
Greater than 400 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-combustible sorbents and providing protection against perchloryl fluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Petroleum Distillates (Naphtha)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_{14} - C_7H_{16} - C_{8H_1}$
- Synonyms: Petroleum naphtha; aliphatic petroleum naphtha; petroleum ether (95 to 115 C); naphtha, petroleum
- Appearance and odor: Colorless liquid with an odor like gasoline and kerosene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for petroleum distillates is 500 parts of petroleum distillates per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of petroleum distillates per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 350 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Petroleum distillates can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to petroleum distillates may cause dizziness, drowsiness, headache, and nausea. They may also cause irritation of the eyes, throat, and skin.

2. Long-term Exposure: Prolonged overexposure may cause drying and cracking of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to petroleum distillates.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to petroleum distillates at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from petroleum distillates exposure.

—Skin disease: Petroleum distillates are skin defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of petroleum distillates might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Although petroleum distillates are not known as liver toxins in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although petroleum distillates are not known as kidney toxins in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapors of petroleum distillates are mild narcotics and mucous membrane irritants. There have been few toxicologic studies, either on animals or man. While 4000 to 7000 ppm are tolerated for 1 hour by human subjects, symptoms of narcosis, such as dizziness and drowsiness, occur at those concentrations. Continuing

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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exposure may produce signs of inebriation, followed by headache or nausea. Exposure at 10,000 to 20,000 ppm is regarded as immediately hazardous to life. The higher boiling fractions may produce irritation of the eyes, nose, and throat in addition to symptoms of mild narcosis. The liquid is a defatting agent, and repeated or prolonged skin contact results in drying and cracking of the skin. No chronic systemic effects have been reported from widespread industrial use. If benzene is present in the distillate, however, the hazard of both acute and chronic poisoning is increased; the presence of elevated phenol in the urine is indicative of benzene exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100 (approximately)
2. Boiling point (760 mm Hg): 30 to 127 C (86 to 260 F)
3. Specific gravity (water = 1): 0.74
4. Vapor density (air = 1 at boiling point of petroleum distillates): 3.4 (approximately)
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 40 mm Hg (approximately)
7. Solubility in water, g/100 g water at 20 C (68 F): 0.04 (approximately)
8. Evaporation rate (butyl acetate = 1): 10 (approximately)

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving petroleum distillates.
4. Special precautions: Petroleum distillates will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −40 to 20 C (−40 to 68 F) (closed cup)
2. Autoignition temperature: 232 to 260 C (450 to 500 F)
3. Flammable limits in air, % by volume: Lower: 1; Upper: 6
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: The odor thresholds of the main constituents of petroleum naphtha (i. e., heptane, octane, pentane, etc.) are below the individual permissible exposure limits.
2. Eye Irritation Level: According to Gafafer, the naphthas irritate the conjunctiva. The American Petroleum Institute states that irritation of the conjunctiva may occur "when the eyes are exposed to high vapor concentrations (of petroleum naphtha) in air. The irritation is mild and transitory." No quantitative information is available concerning the threshold of eye irritation, however.
3. Evaluation of Warning Properties: Since the odor of each of the main constituents of petroleum naphtha is detectable at concentrations below the respective permissible exposure limits, petroleum naphtha is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of petroleum distillates vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure petroleum distillates may be used. An analytical method for petroleum distillates is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid petroleum distillates.

- Clothing wet with liquid petroleum distillates should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of petroleum distillates from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the petroleum distillates, the person performing the operation should be informed of petroleum distillates' hazardous properties.
- Any clothing which becomes wet with liquid petroleum distillates should be removed immediately and not reworn until the petroleum distillates are removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid petroleum distillates may contact the eyes.

SANITATION

- Skin that becomes wet with liquid petroleum distillates should be promptly washed or showered with soap or mild detergent and water to remove any petroleum distillates.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to petroleum distillates may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during degreasing operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as solvents in rubber industry during manufacture of water-proof cloth, shoe adhesives, and rubber tires	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as extractants; use in preparation of paint, varnish, and lacquer as solvents, diluents, or thinners; use as solvents in pesticides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during dry cleaning operations	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If petroleum distillates get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If petroleum distillates get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If petroleum distillates soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of petroleum distillates, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If petroleum distillates have been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If petroleum distillates are spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Petroleum distillates should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Petroleum distillates may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PETROLEUM DISTILLATES (NAPHTHA)

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phenol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_5OH
- Synonyms: Carbolic acid; monohydroxybenzene
- Appearance and odor: Colorless to pink solid or thick liquid with a characteristic, sweet, tarry odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenol is 5 parts of phenol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 19 milligrams of phenol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 20 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 60 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Phenol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenol can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Phenol has a marked corrosive effect on any tissue. When it comes in contact with the eyes, it may cause severe damage and blindness. On contact with the skin, it does not cause pain but causes a whitening of the exposed area. If the chemical is not removed promptly, it may cause a severe burn or systemic poisoning. Systemic effects may occur from any route of exposure, especially after skin contact.

2. Long-term Exposure: Repeated or prolonged exposure to phenol may cause chronic phenol poisoning. The symptoms of chronic poisoning include vomiting, difficulty in swallowing, diarrhea, lack of appetite, headache, fainting, dizziness, dark urine, mental disturbances, and possibly a skin rash. Liver damage and discoloration of the skin may occur.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phenol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phenol at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders or abnormalities of the skin, respiratory tract, liver, or kidneys would be expected to be at increased risk from exposure. Examination of the liver, kidneys, and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Darkening of the urine has occurred in persons exposed to phenol after accidental ingestion or skin contact. A urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Urinary phenol is useful if good individual background levels are available.

—Liver function tests: Since liver damage has been observed in humans exposed to phenol, a profile of liver function should be performed by using a medically acceptable array of biochemical tests.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Phenol in the vapor form or in solution is an irritant to the eyes, mucous membranes, and skin; systemic absorption causes central nervous system effects as well as liver and kidney damage. Sudden collapse is characteristic of gross overexposure. In animals, prolonged inhalation of the vapor at 30 to 60 ppm induced respiratory difficulty, lung damage, and paralysis. Systemic absorption by animals caused muscle twitching and severe convulsions. There are no reports of human fatalities from inhalation of the vapor, although one case of severe poisoning has been reported. Ingestion of lethal amounts (as little as 1 g) cause severe burns of the mouth and throat, marked abdominal pain, cyanosis, muscular weakness, collapse, coma, and death; tremors, convulsions, or muscle twitching were occasionally observed but were not severe. A laboratory technician repeatedly exposed to unknown vapor concentrations and liquid spilled on the skin developed anorexia, weight loss, weakness, muscle aches and pain, and dark urine; during several months of nonexposure there was gradual improvement in his condition, but after brief reexposure he suffered an immediate worsening of symptoms with prompt darkening of the urine and tender enlargement of the liver. Brief intermittent industrial exposures to vapor concentrations of 48 ppm of phenol (accompanied by 8 ppm of formaldehyde) caused marked irritation of eyes, nose, and throat. Concentrated phenol solutions are severely irritating to the human eye and cause conjunctival swelling; the cornea becomes white and hypesthetic; loss of vision has occurred in some cases. Solutions of phenol have a marked corrosive action on any tissue on contact; on skin, there is local anesthesia and a white discoloration, and the area may subsequently become gangrenous; severe dermatitis will result from contact with dilute solutions, and prolonged exposure may result in ochronosis. In workers making phenol-formaldehyde plastic, the urinary level of total phenol, free plus conjugated, was proportional to the air concentration of phenol up to 12.5 mg/m^3 of workroom air. Mice were treated twice weekly for 72 weeks by application of 1 drop of a 10% solution of phenol in benzene to the shaved dorsal skin; after 52 weeks of treatment there were papillomas in 5 of 14 mice, and 1 fibrosarcoma appeared at 58 weeks.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 94.11
2. Boiling point (760 mm Hg): 182 C (359 F)
3. Specific gravity (water = 1): 107 (solid); 1.05 (liquid)
4. Vapor density (air = 1 at boiling point of phenol): 3.24
5. Melting point: 41 C (106 F)
6. Vapor pressure at 20 C (68 F): 0.36 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.4
8. Evaporation rate (butyl acetate = 1): Less than 0.01

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers (especially calcium hypochlorite) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving phenol.
4. Special precautions: Liquid phenol will attack some forms of plastics, rubber, and coatings. Hot liquid phenol will attack aluminum, magnesium, lead, and zinc metals.

- **Flammability**

1. Flash point: 79 C (174 F) (closed cup)
2. Autoignition temperature: 715 C (1319 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.6
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Summer reports that the odor threshold of phenol is 3 ppm; the Manufacturing Chemists Association reports 0.3 ppm; Thienes and Haley report 5 ppm.
2. Irritation Levels: The *Documentation of TLV's* reports that intermittent exposures to 48 ppm phenol have been observed to produce eye, nose, and throat irritation. Formaldehyde was also present in this atmosphere at a concentration of 8 ppm. The Respirator Review Committee considers the source of the eye irritation to be the 8 ppm formaldehyde rather than the phenol.
3. Evaluation of Warning Properties: Since the odor threshold of phenol is at or below the permissible exposure limit, phenol is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of phenol. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of phenol in a bubbler containing sodium hydroxide, followed by treatment with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure phenol may be used. An analytical method for phenol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid phenol or liquids containing phenol.
- If employees' clothing has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phenol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phenol, the person performing the operation should be informed of phenol's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solid or liquid phenol or liquids containing phenol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phenol should be removed immediately and not reworn until the phenol is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid phenol or liquids containing phenol contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid phenol or liquids containing phenol, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phenol should be immediately washed or showered with soap or mild detergent and water to remove any phenol.
- Any clothing which becomes wet with liquid phenol or liquids containing phenol should be removed immediately and not reworn until the phenol is removed from the clothing.
- Eating and smoking should not be permitted in areas where solid or liquid phenol or liquids containing phenol are handled, processed, or stored.
- Employees who handle solid or liquid phenol or liquids containing phenol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phenol may occur and control methods which may be effective in each case:

Operation	Controls
Application and curing of bonding resin in plywood manufacture; application and curing of molding resins in manufacture of molded articles, such as	Process enclosure; local exhaust ventilation; personal protective equipment

electrical appliances, automotive parts, foundry sand molds, and utensil handles; manufacture of friction materials, bonded abrasives, coated abrasives, wood particle board, and insulation materials	
Use in industrial coatings in drum and can linings, milk and beer-processing equipment, water tanks and air-conditioning equipment, decorative laminates, and textile coatings	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of thermosetting phenolic resins, epoxy, polycarbonate, phenoxy, and polysulfone; synthesis of aprolactam for use in nylon 6 fibers, plastics, and films	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of agricultural chemicals and intermediates; synthesis of pharmaceuticals, rubber and plastic plasticizers, antioxidants, curing agents, and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of stabilizers and preservatives for dyes, perfumes, and fungicides	Process enclosure; local exhaust ventilation; personal protective equipment
Use during solvent refining of lubrication oil and wax; use in synthesis of additives for gasoline and lubricating fluids and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of intermediates in polyester production; production of corrosion-resistant polyester and polyester polyols; use in synthesis of dye intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of surface-active agents and detergent intermediates; in synthesis of explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of disinfectant agents and products for industrial and household use	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of synthetic cresols and xylenols	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid or liquid phenol or liquids containing phenol get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid phenol or liquids containing phenol get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid phenol or liquids containing phenol penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of phenol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solid or liquid phenol or liquids containing phenol have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phenol is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill.
2. If in the solid form, for small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.
3. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

- Waste disposal methods:

Phenol may be disposed of:

1. If in the solid form, by making packages of phenol in paper or other flammable material and burning in a suitable combustion chamber, or by dissolving phenol in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.
2. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill, or by atomizing the liquid in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PHENOL

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of phenol; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for p-Phenylene Diamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_8N_2$
- Synonyms: p-Diaminobenzene; 1,4-diaminobenzene
- Appearance: White to light purple or brown solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-phenylene diamine is 0.1 milligram of p-phenylene diamine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Phenylene diamine can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: p-Phenylene diamine may cause irritation of the throat.

2. Long-term Exposure: Repeated or prolonged exposure may cause allergy with asthma or skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to p-phenylene diamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-phenylene diamine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to p-phenylene diamine would be expected to be at increased risk from exposure. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

p-Phenylene diamine dust is a skin and respiratory system sensitizer and may produce bronchial asthma and dermatitis in exposed workers. In cats, the minimal fatal peroral dose was 0.1 g/kg. Solutions administered orally or parenterally to animals caused a peculiar and selective edema of the conjunctivae, nose, lips, tongue, and neck. Inflammatory reactions of the pharynx and larynx have been reported in workers. Very small quantities of the dust have caused asthmatic attacks in workers after periods of exposure ranging from 3 months to 10 years. A dilute aqueous solution placed in the eye of a rabbit caused mild transient conjunctival edema. This compound may cause contact dermatitis through sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 108.1
2. Boiling point (760 mm Hg): 267 C (512 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of p-phenylene diamine): 3.71
5. Melting point: 141 C (286 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 4.7
8. Evaporation rate (butyl acetate = 1): Data not

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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available

- **Reactivity**

1. Conditions contributing to instability: Heat; light
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving p-phenylene diamine.
4. Special precautions: None

- **Flammability**

1. Flash point: 155.5 C (312 F) (closed cup)
2. Autoignition temperature: Data not available
3. Minimum explosive concentration: 0.025 g/l
4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of p-phenylene diamine.
2. Eye Irritation Level: Gleason reports that p-phenylene diamine in the eye produces "chemosis, lacrimation, exophthalmos ophthalmia, and even permanent blindness." Kirk and Othmer report that p-phenylene diamine "is responsible for keratoconjunctivitis, swollen conjunctiva, and eczema of the eyelids." Grant provides similar information, but no quantitative data are given.
3. Evaluation of Warning Properties: p-Phenylene diamine is treated as material with poor warning properties, since no quantitative data are available relating warning properties to air concentrations of p-phenylene diamine.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for p-phenylene diamine had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with p-phenylene diamine or liquids containing p-phenylene diamine, where skin contact may occur.
- If employees' clothing may have become contaminated with p-phenylene diamine or liquids containing p-phenylene diamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-phenylene diamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of p-phenylene diamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-phenylene diamine, the person performing the operation should be informed of p-phenylene diamine's hazardous properties.
- Non-impervious clothing which becomes contaminated with p-phenylene diamine should be removed promptly and not reworn until the p-phenylene diamine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where p-phenylene diamine or liquids containing p-phenylene diamine may contact the eyes.

SANITATION

- Workers subject to skin contact with p-phenylene diamine or liquids containing p-phenylene diamine should wash with soap or mild detergent and water any areas of the body which may have contacted p-phenylene diamine at the end of each work day.
- Skin that becomes contaminated with p-phenylene diamine should be promptly washed or showered with soap or mild detergent and water to remove any p-phenylene diamine.

- Eating and smoking should not be permitted in areas where p-phenylene diamine or liquids containing p-phenylene diamine are handled, processed, or stored.
- Employees who handle p-phenylene diamine or liquids containing p-phenylene diamine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-phenylene diamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in dye and dyestuff intermediates for fur, hair, leather, cotton, and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in photographic application as a fine-grain developing agent, for preparation of color developers, and for photochemical measurements; use in polymer technology for manufacture of Fiber B, and as a cross-linking agent; use as a catalyst; use in preparation of epoxy resins, synthetic fibers, heat-resistant polymers, and coatings for leather, paper, and textiles	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in rubber technology for natural and synthetic rubber for vulcanization, as an antioxidant, accelerator, and stabilizer	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in preparation of antioxidants for petroleum fuels; preparation of grease thickeners, electrical insulators, and rust removers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in laboratory as an analytical reagent, and as a special solvent	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If p-phenylene diamine or liquids containing p-phenylene diamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If p-phenylene diamine or liquids containing p-phenylene diamine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If p-phenylene diamine or liquids containing p-phenylene diamine penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of p-phenylene diamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When p-phenylene diamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If p-phenylene diamine is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

p-Phenylene diamine may be disposed of:

1. By making packages of p-phenylene diamine in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-phenylene diamine in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR p-PHENYLENE DIAMINE

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m³**
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 25 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against p-phenylene diamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phenyl Ether

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_6H_5)_2O$
- Synonyms: Diphenyl ether; diphenyl oxide
- Appearance and odor: Colorless solid or liquid with a somewhat disagreeable odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenyl ether is 1 part of phenyl ether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7 milligrams of phenyl ether per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenyl ether can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to phenyl ether vapor or mist may cause nausea and irritation of the eyes and nose.

2. Long-term Exposure: Prolonged or repeated exposure to undiluted phenyl ether liquid may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phenyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phenyl ether at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from phenyl ether exposure.

—Skin disease: Phenyl ether can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although phenyl ether is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although phenyl ether is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of phenyl ether might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Phenyl ether irritates the skin and eyes and has an objectionable odor which may cause nausea. The liquid appears to be low in oral toxicity, but little information on its physiologic effects is available. The acute lethal dose for rats and guinea pigs is 4 g/kg. Animals that survived oral doses of 1 to 2 g/kg showed some injury to the liver, kidneys, spleen, and thyroid. No chronic systemic effects have been reported in humans.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 170.2
2. Boiling point (760 mm Hg): 259 C (498 F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of phenyl ether): 5.86
5. Melting point: 27 C (81 F) (maximum value)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0021
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving phenyl ether.
4. Special precautions: Phenyl ether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 115 C (239 F) (closed cup)
2. Autoignition temperature: 620 C (1148 F)
3. Flammable limits in air, % by volume: Lower: 0.8; Upper: 1.5
4. Extinguishant: Foam dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for phenyl ether of 0.01 ppm, and Stern reports 0.001 ppm
2. Eye Irritation Level: The *Documentation of TLV's* states that "effects of . . . eye application (of phenyl ether) resemble closely those found for the eutectic mixture with diphenyl; phenyl ether in concentrated, prolonged exposures is somewhat irritating but is not so in dilution." The phenyl ether-diphenyl mixture is known to produce eye irritation at 3-4 ppm (Grant).
3. Evaluation of Warning Properties: Since the odor threshold of phenyl ether is lower than the permissible exposure limit, this substance is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of phenyl ether vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure phenyl ether may be used. An analytical method for phenyl ether is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid or solid phenyl ether.
- Non-impervious clothing which becomes contaminated with liquid or solid phenyl ether should be removed promptly and not reworn until the phenyl ether is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid phenyl ether may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid or solid phenyl ether should be promptly washed or showered with soap or mild detergent and water to remove any phenyl ether.
- Employees who handle liquid or solid phenyl ether should wash their hands thoroughly with soap or mild

detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phenyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a high-temperature, heat-transfer medium as Dowtherm A, Thermax, Diphyl, and Gilotherm	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an organic intermediate in organic synthesis resulting in epoxy resins, other phenol-based heat-resistant resins, polysulfone resins, high-temperature lubricants, surfactants, specialty plasticizers, varnishes, phenol-formaldehyde resins, artificial sweetners, insecticides, preservatives, fire retardants, and adhesives	General dilution ventilation; personal protective equipment
Use as an odorant in the manufacture of soaps and perfumes; use as a flavoring agent in manufacture of food products	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phenyl ether gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phenyl ether gets on the skin, promptly wash the contaminated skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleanser. If phenyl ether soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleansers. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of phenyl ether, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phenyl ether has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phenyl ether is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb or scoop up on paper. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed; however, if this is not practical, collect, dissolve in an appropriate solvent, and atomize in a suitable combustion chamber.

- Waste disposal method:

Phenyl ether may be disposed of by dissolving in appropriate solvent and atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR PHENYL ETHER

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s) with a full facepiece and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister with a full facepiece and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 ppm or less	A powered air-purifying chemical cartridge respirator with a full facepiece, organic vapor cartridge, and high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phenyl Ether-Biphenyl Mixture

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_6H_5)_2O$ and $C_6H_5C_6H_5$
- Synonyms: Dowtherm A; diphenyl oxide-diphenyl mixture
- Appearance and odor: Straw-colored liquid that darkens on use with an aromatic, somewhat disagreeable odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenyl ether-biphenyl mixture is 1 part of phenyl ether-biphenyl mixture per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7 milligrams of phenyl ether-biphenyl mixture per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for phenyl ether-biphenyl mixture from 1 ppm to 0.5 ppm as a vapor.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenyl ether-biphenyl mixture can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to phenyl ether-biphenyl mixture may cause irritation of the eyes, nose, and skin. It may also cause nausea.

2. Long-term Exposure: Repeated or prolonged contact may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phenyl ether-biphenyl mixture.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phenyl ether-biphenyl mixture at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from phenyl ether-biphenyl mixture exposure.

—Skin disease: Phenyl ether-biphenyl mixture can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although phenyl ether-biphenyl mixture is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although phenyl ether-biphenyl mixture is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of phenyl ether-biphenyl mixture might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Phenyl ether-biphenyl mixture is primarily an irritant to

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the eyes, skin, and upper respiratory tract. Repeated 8-hour exposures at 182 mg/m^3 of a vapor-mist mixture were lethal to some animals within 1-½ months. Long-term (6-month) studies of four species at 7 to 10 ppm showed no significant adverse effects, although these concentrations are extremely nauseating to human subjects and painfully irritating to the eyes and nose. While 1 ppm is tolerable to most individuals, the odor at 0.1 ppm may be objectionable to some. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 166 (average)
2. Boiling point (760 mm Hg): 257 C (495 F)
3. Specific gravity (water = 1): 1.05 to 1.07
4. Vapor density (air = 1 at boiling point of phenyl ether-biphenyl mixture): 5.7 (average)
5. Melting point: 12 C (54 F)
6. Vapor pressure at 25 C (77 F): 0.08 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0014
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving phenyl ether-biphenyl mixture.
4. Special precautions: Phenyl ether-biphenyl mixture will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 124 C (255 F) (open cup)
2. Autoignition temperature: 621 C (1150 F)
3. Flammable limits in air, % by volume: Lower: 0.5; Upper: 6.2 (at 500 F)
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states, "Experience with human subjects has indicated that concentrations of vapors of Dowtherm A ranging from 0.1 to 1 ppm are readily detected by the olfactory organs and are unpleasant, sometimes producing nausea." The *Documentation of TLV's* states that a TLV of 1 ppm is recommended "to prevent disagreeable, nauseating odor for the majority of exposed workers. As little as 0.1 ppm may be objectionable to some sensitized, exposed individuals. The TLV of 1 ppm is sufficiently low to prevent serious toxic effects but may not eliminate all objectionable symptoms."
2. Irritation Levels: Grant states that "when concentrations of 3 or 4 ppm in air are reached, there is irritation of the eyes, nose, and throat."
3. Evaluation of Warning Properties: Through its odor and irritant effects, phenyl ether-biphenyl mixture can be detected at a concentration within 3 times the permissible exposure limit. For the purposes of this guideline, this mixture is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of phenyl ether-biphenyl mixture in an adsorption tube containing silica gel, followed by desorption with benzene, and gas chromatographic analysis. An analytical method for phenyl ether-biphenyl mixture is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid or solid phenyl ether-biphenyl mixture.

- Non-impervious clothing which becomes contaminated with liquid or solid phenyl ether-biphenyl mixture should be removed promptly and not reworn until the phenyl ether-biphenyl mixture is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid phenyl ether-biphenyl mixture may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid or solid phenyl ether-biphenyl mixture should be promptly washed or showered with soap or mild detergent and water to remove any phenyl ether-biphenyl mixture.
- Employees who handle liquid or solid phenyl ether-biphenyl mixture should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phenyl ether-biphenyl mixture may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical, petroleum, and nuclear industry as a high-transfer medium used in heating and cooling processes— marked as Dowtherm A, Termax, Diphyl, and Gilotherm	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a dye carrier (dyeing aid) for printing and dyeing polyester textiles	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phenyl ether-biphenyl mixture gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phenyl ether-biphenyl mixture gets on the skin, promptly wash the contaminated skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleansers. If phenyl ether-biphenyl mixture soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleaners. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of phenyl ether-biphenyl mixture, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phenyl ether-bisphenyl mixture has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phenyl ether-biphenyl mixture is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb or scoop up on paper. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities may be reclaimed; however, if this is not practical, dissolve in an appropriate solvent and atomize in a suitable combustion chamber.

- Waste disposal method:

Phenyl ether-biphenyl mixture may be disposed of by dissolving in an appropriate solvent and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PHENYL ETHER-BIPHENYL MIXTURE

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s) with a full facepiece and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister with a full facepiece and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 ppm or less	A powered air-purifying chemical cartridge respirator with a full facepiece, organic vapor cartridge, and high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

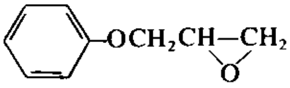
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PHENYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about phenyl glycidyl ether (PGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_9H_{10}O_2$
- **Structure:**



- **Synonyms:** Glycidyl phenyl ether; PGE; phenyl 2,3-epoxypropyl ether; 1,2-epoxy-3-phenoxypropane; phenoxy-propene oxide
- **Identifiers:** CAS 122-60-1; RTECS TZ3675000; DOT not assigned
- **Appearance:** Colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 150.17
2. Boiling point (at 760 mmHg): 245 °C (473 °F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of PGE): 4.37
5. Melting point: 3.5 °C (38 °F)
6. Vapor pressure at 25 °C (77 °F): 0.01 mmHg
7. Solubility in water, g/100 g water at 20 °C (68 °F): 0.24
8. Saturation concentration in air (approximate) at 25 °C (77 °F): 0.0013% (13 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with amines, strong acids, and strong bases may cause polymerization with the liberation of heat and spattering. Exposure to light and air may result in the formation of explosive peroxides.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving PGE.
3. Caution: PGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 120 °C (248 °F) (closed cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class IIIB Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, PGE should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for PGE is 10 parts of PGE per million parts of air (ppm) [60 milligrams of PGE per cubic meter air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 1 ppm (5 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 1 ppm (6 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for phenyl glycidyl ether

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	10	60
NIOSH REL, ceiling (15 min)	1	5
ACGIH TLV® TWA	1	6

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

- **Routes of exposure**

PGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute dermal or oral administration of PGE to rats and mice caused tissue destruction (necrosis) at the site of administration, liver damage, and central nervous system (CNS) depression. Subchronic inhalation of PGE by rats produced equivocal evidence of testicular degeneration. Chronic inhalation of PGE by rats produced nasal cancer. NIOSH will continue to monitor the research regarding PGE to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to PGE can cause irritation of the eyes, nose, respiratory tract, and skin.
2. *Long-term (chronic):* Exposure to PGE can cause defatting and drying of the skin, dermatitis, blisters, edema, rash, eczema, and skin sensitization; cross sensitization with other glycidyl ethers can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to PGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and reproductive, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to PGE at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to PGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, and reproductive, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of PGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

- **Method**

Sampling and analysis may be performed by collecting PGE vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure PGE may also be used if available. A detailed sampling and analytical method for PGE may be found in the *NIOSH Manual of Analytical Methods* (method number S74).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with PGE.

Workers should be provided with and required to use splash-proof safety goggles where PGE may come in contact with the eyes.

SANITATION

Clothing which is contaminated with PGE should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of PGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of PGE's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with PGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle PGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to PGE may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for phenyl glycidyl ether

Operations	Controls
During use as a coupling agent, catalyst, or reactive diluent in curing rubber, thermostable epoxy resins, tire cord, and electric insulating materials	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a stabilizer of halogenated compounds; during use in the treatment of fabric	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a copolymer in the production of epoxy polymers; during use as chemical intermediate	Process enclosure, local exhaust ventilation, general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to PGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If PGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to PGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If PGE gets on the skin, wash it immediately with soap and water. If PGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If PGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing PGE, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from PGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing PGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. PGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. PGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for phenyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 25 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 50 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 500 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 500 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (5 mg/m^3) (ceiling).

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PHENYLHYDRAZINE

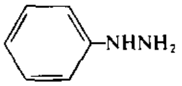
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about phenylhydrazine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_8N_2$
- **Structure:**



- **Synonyms:** Hydrazinobenzene, hydrazine-benzene
- **Identifiers:** CAS 100-63-0; RTECS MV8925000; DOT 2572, label required: "Poison"
- **Appearance and odor:** Pale yellow crystals or oily liquid with a faint aromatic odor; color darkens upon exposure to air and light

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 108.16
2. Boiling point (at 760 mmHg): 243.5 °C (471 °F) with decomposition
3. Specific gravity (water = 1): 1.0978
4. Vapor density (air = 1 at boiling point of phenylhydrazine): 3.7
5. Melting point: 19.6 °C (68 °F)
6. Vapor pressure at 25 °C (77 °F): 0.04 mmHg
7. Slightly soluble in water
8. Evaporation rate (butyl acetate = 1): 0.4
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 50 ppm
10. Ionization potential: 7.66 eV

- **Reactivity**

1. Incompatibilities: Phenylhydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving phenylhydrazine.
3. Caution: Phenylhydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 88 °C (190 °F) (closed cup)
2. Autoignition temperature: 174 °C (345 °F)
3. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or large quantities of coarse water spray
4. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)
5. Caution: Phenylhydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth, or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for phenylhydrazine is 5 parts of phenylhydrazine per million parts of air (ppm) [22 milligrams of phenylhydrazine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that phenylhydrazine be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.14 ppm (0.6 mg/m^3) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated phenylhydrazine as an A2 substance (suspected hu-

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man carcinogen) having an assigned threshold limit value (TLV®) of 5 ppm (20 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short term exposure limit (STEL) is 10 ppm (45 mg/m³) (Table 1).

Table 1.— Occupational exposure limits for phenylhydrazine

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	5	22
NIOSH REL (Ca)† ceiling (120 min)	0.14	0.6
ACGIH TLV® TWA (Skin) (A2)§	5	20
STEL (Skin) (A2)	10	45

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

† (Ca): NIOSH recommends treating as a potential human carcinogen.

§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenylhydrazine may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute subcutaneous or intraperitoneal injection of phenylhydrazine hydrochloride in mice, rats, or dogs caused deficient oxygenation of the blood (cyanosis), breathing difficulty (dyspnea), convulsions, severe hemolytic anemia, or degenerative lesions of the liver and kidneys. Subchronic oral administration of phenylhydrazine to mice produced tumors of the blood vessels and cancer of the lungs. Phenylhydrazine injected into pregnant rats reduced certain learning abilities in the offspring by inducing severe neonatal jaundice and anemia.
2. *Effects on humans:* Exposure of workers to phenylhydrazine has caused hemolytic anemia.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to phenylhydrazine can cause vomiting, diarrhea, fatigue, headache, and irritation and itchiness of the eyes and skin.
2. *Long-term (chronic):* Repeated skin contact with phenylhydrazine can cause skin sensitization and eczematous dermatitis with redness, swelling, and rash.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to phenylhydrazine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and hematopoietic (blood-cell forming), nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS). There is little information available on the risk to workers with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to phenylhydrazine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to phenylhydrazine.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to phenylhydrazine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and hematopoietic, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to phenylhydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of phenylhydrazine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 120-minute sample or a series of consecutive samples that total 120 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting phenylhydrazine with tubes containing sulfuric-acid-coated silica and analyzing by gas chromatography. Direct-reading devices calibrated to measure phenylhydrazine may also be used if available. A detailed sampling and analytical method for phenylhydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with phenylhydrazine.

SANITATION

Clothing which is contaminated with phenylhydrazine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of phenylhydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of phenylhydrazine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with phenylhydrazine should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle phenylhydrazine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to phenylhydrazine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for phenylhydrazine

Operations	Controls
During the manufacture of phenylhydrazine; during maintenance of manufacturing and storage equipment	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the manufacture of pharmaceuticals, photographic developers, polymethene dyes, and nitron (a stabilizer for explosives)	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an analytical reagent, intermediate in inorganic synthesis, or reducing agent	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to phenylhydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If phenylhydrazine gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to phenylhydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If phenylhydrazine gets on the skin, wash it immediately with soap and water. If phenylhydrazine penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If phenylhydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing phenylhydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing phenylhydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Phenylhydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for phenylhydrazine

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Phosdrin

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3O)_2PO_2C(CH_3) = CHCOOCH$
- Synonyms: Mevinphos (R); 2-carbomethoxy-1-methylvinyl dimethyl phosphate
- Appearance and odor: Colorless or yellow liquid with a weak odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosdrin is 0.1 milligram of phosdrin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosdrin can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of phosdrin, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing phosdrin, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur, usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to the above symptoms, weakness, generalized twitching and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heartbeat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to phosdrin may make a person more susceptible to the effects of this and related chemicals. Repeated exposure to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosdrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosdrin at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Cholinesterase determination: Phosdrin (Mevinphos) causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to any new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determi-

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nation which should be performed quarterly or at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Phosdrin (Mevinphos) is an anticholinesterase agent; absorption may occur from inhalation of the vapor or mist, from skin absorption of the liquid, or from ingestion. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscle, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms may occur promptly or may be delayed for up to 12 hours. After inhalation, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects, such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for several weeks after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects. In two cases of moderate intoxication from Mevinphos, urinary excretion of dimethylphosphate (a metabolite of Mevinphos) was almost complete 50 hours after exposure; although a number of other organophosphorus pesticides also yield dimethylphosphate, the presence of significant amounts of this metabolite in the urine may be useful in estimating the absorption of Mevinphos.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 224
2. Boiling point (760 mm Hg): 325 C (617 F)
3. Specific gravity (water = 1): 1.24
4. Vapor density (air = 1 at boiling point of phosdrin): Not applicable
5. Melting point: −56 C (−69 F) (pour point)
6. Vapor pressure at 20 C (68 F): 0.003 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Phosdrin decomposes vigorously when heated above 300 C (572 F) and will cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid mist and carbon monoxide) may be released in a fire involving phosdrin.
4. Special precautions: Phosdrin will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 79 C (175 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of phosdrin.
2. Eye Irritation Level: Phosdrin is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, phosdrin is treated as a material with poor warning properties. The concentration of phosdrin in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for phosdrin is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with phosdrin.
- Clothing which has had any possibility of being contaminated with phosdrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phosdrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosdrin, the person performing the operation should be informed of phosdrin's hazardous properties.
- Where there is any possibility of exposure of an employee's body to phosdrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phosdrin should be removed immediately and not reworn until the phosdrin is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid phosdrin contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to phosdrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phosdrin should be immediately washed or showered to remove any phosdrin.
- Eating and smoking should not be permitted in areas where phosdrin is handled, processed, or stored.
- Employees who handle phosdrin should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosdrin may occur and control methods which may be effective in each case:

Operation	Controls
Application as an insecticide on agricultural crops, fruits, and vegetables; for ornamentals in greenhouses; use as an insecticide in sewage treatment plants	Personal protective equipment
Formulation and mixing for insecticidal application	Local exhaust ventilation; personal protective equipment
Manufacture of phosdrin	Local exhaust ventilation; personal protective equipment; process enclosure

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phosdrin or phosdrin mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phosdrin or phosdrin mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If phosdrin or phosdrin mists penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of phosdrin, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phosdrin has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phosdrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Phosdrin may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR PHOSDRIN

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate or Vapor Concentration	
1 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of phosdrin; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 40 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Phosgene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $COCl_2$
- Synonyms: Carbonyl chloride; carbon oxychloride; chloroformyl chloride
- Appearance and odor: Colorless liquid or gas with a sweet odor like hay at low concentrations and a sharp pungent odor at high concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosgene is 0.1 part of phosgene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of phosgene per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be changed to 0.1 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.2 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Phosgene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosgene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Phosgene, after a minute or so of exposure to low concentrations, may cause cough and discomfort in the chest and irritation of the nose and throat. Higher concentrations may cause painful coughing with respiratory irritation. Phosgene may cause pulmonary edema with coughing, shortness of breath, and production of frothy sputum. This can be fatal. Pulmonary edema may occur many hours after exposure. The gas may irritate the eyes. If liquid phosgene is splashed on the skin or eyes, it may cause burns.

2. Long-term Exposure: No known effect

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosgene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosgene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Phosgene may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec and 25— 75): Phosgene is reported to cause pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Phosgene gas is a severe respiratory irritant. The least concentration claimed to be capable of causing immediate irritation of the human throat is 3 ppm; 4 ppm causes immediate irritation of the eyes; 4.8 ppm causes cough; brief exposure to 50 ppm may be rapidly fatal. With moderate exposure, the presenting symptoms are often a dryness or a burning sensation in the throat, vomiting, pain in the chest, and dyspnea. The onset of symptoms

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of severe respiratory distress may be delayed for up to 72 hours, the latent interval depending upon the concentration and duration of exposure. The delayed onset of pulmonary edema is characterized by cough, abundant quantities of foamy sputum, progressive dyspnea, and severe cyanosis. Pulmonary edema may progress to pneumonia, and cardiac failure may intervene. The gas in concentrations of 1 to 2 ppm causes eye discomfort, and higher concentrations are likely to cause lacrimation and conjunctivitis; splashes of liquid phosgene in the eye may produce severe irritation. Skin contact with the liquid may cause severe burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.9
2. Boiling point (760 mm Hg): 8.2 C (46.7 F)
3. Specific gravity (water = 1): 1.4
4. Vapor density (air = 1 at boiling point of phosgene): 3.4
5. Melting point: −128 C (−198 F)
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts with water
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with moisture causes slow decomposition to form hydrogen chloride with carbon dioxide.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and carbon monoxide) may be released when phosgene decomposes, but these gases are less toxic than phosgene itself.
4. Special precautions: Liquid phosgene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The odor threshold of phosgene has been reported as 0.125 ppm by the ILO, 0.5 to 1.0 ppm by Thienes and Haley, and 0.5 ppm by both Patty and May. The MCA *states in its Chemical Safety Data Sheet*, however, that "the gas has the ability to condition the sense of smell so that the characteristic odor can be detected only briefly at the time of initial exposure."
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the vapor of phosgene in concentrations of 1 to 2 ppm causes a scratchy sensation of the eyes, and higher concentrations are likely to cause lacrimation and conjunctivitis." They also state that within a few minutes 5 ppm might cause eye irritation.
3. Other Information: Patty notes that concentrations below 10 ppm produce mild irritation of the mucous membranes, and concentrations above 10 ppm can produce serious irritation. At 2 ppm, irritation of the nose and throat is "barely detectable." The *Documentation of TLV's* reports that 3 ppm has been claimed to be the lowest concentration causing irritation of the throat. Stecher notes, however, that phosgene is "an insidious poison, as it is not irritating immediately, even when fatal concentrations are inhaled."
4. Evaluation of Warning Properties: Since phosgene has the ability "to condition the sense of smell so that the characteristic odor can be detected only briefly at the time of initial exposure," and since the threshold of eye, nose, and throat irritation are many times higher than the permissible exposure limit, phosgene has been treated as a material with poor warning properties. In addition, according to Stecher, the irritant effects of phosgene are delayed, giving no warning that harmful concentrations are being inhaled.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of phosgene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of phosgene in a midget impinger containing a solution of nitrobenzylpyridine, followed by colorimetric analysis. An analytical method for phosgene is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, full facepiece respirator, gloves, face shields (eight-inch minimum), and other appropriate protective clothing where skin contact with liquid phosgene may occur.
- Where there is any possibility of exposure of an employee's body to liquid phosgene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes wet with liquid phosgene should be removed immediately while using quick drenching facilities and not reworn until the phosgene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid phosgene contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to phosgene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid phosgene should be immediately washed or showered with very large quantities of water to remove any phosgene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosgene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during open-flame cutting of certain metals in presence of chlorinated hydrocarbons	Insolation of operations from chlorinated hydrocarbons; local exhaust ventilation; personal protective equipment
Liberation from synthesis of isocyanates in manufacture of polyurethane plastics; alkyl isocyanates in pesticide manufacture; polycarbonated resins for molded plastics, dyestuffs, and pharmaceuticals	Process enclosure; local exhaust ventilation
Liberation during fire-extinguishing with agents containing chlorinated hydrocarbons	Material substitution; personal protective equipment
Liberation during sand bleaching operations in glass manufacture	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phosgene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phosgene gets on the skin, immediately flush the contaminated skin with large quantities of water. If phosgene soaks through the clothing, remove the clothing immediately while using a quick drenching facility and flush the skin with large quantities of water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of phosgene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If phosgene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phosgene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty. Water spray may be used to knock down the vapor.
3. If in the liquid form, allow to vaporize.

- Waste disposal methods:

Phosgene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on phosgene, look up phosgene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Phosgene (February 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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RESPIRATORY PROTECTION FOR PHOSGENE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against phosgene. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phosphine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: PH_3
- Synonyms: Hydrogen phosphide; phosphorus hydride; phosphorated hydrogen
- Appearance and odor: Colorless gas with a characteristic fishy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphine is 0.3 part of phosphine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of phosphine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphine can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of phosphine may cause coughing, shortness of breath, and severe breathing difficulty. This breathing difficulty may not appear until several hours after exposure has ceased. It may also cause thirst, nausea, vomiting, stomach pain, diarrhea, back pain, a feeling of coldness, fainting, and death.

2. Long-term Exposure: Not known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from phosphine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of phosphine might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Phosphine gas is a severe pulmonary irritant and an acute systemic poison; it has caused both sudden death and delayed death due to pulmonary edema. Workers exposed intermittently to concentrations up to 35 ppm, but averaging below 10 ppm, complained of nausea, vomiting, diarrhea, chest tightness and cough, headache, and dizziness; no evidence of cumulative effects was noted. Single severe exposures cause similar signs and symptoms, as well as excessive thirst, muscle pain, chills, sensation of pressure in the chest, dyspnea, syncope, and stupor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 34.04
2. Boiling point (760 mm Hg): −87.8 C (−126 F)
3. Specific gravity (water = 1): Liquid = 0.75 at boiling point
4. Vapor density (air = 1 at boiling point of phosphine): 1.17
5. Melting point: −134 C (−209 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere

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7. Solubility in water, g/100 g water at 20 C (68 F): 0.04

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Overheated cylinders may explode.

2. Incompatibilities: Contact with air or any other oxidizer such as chlorine, etc., will cause ignition of phosphine. Phosphine reacts with acids, halogenated hydrocarbons, and moisture.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of phosphorus, phosphoric acid mist, and hydrogen) may be released in a fire involving phosphine.

4. Special precautions: Phosphine is an unusually reactive and poisonous substance, and is usually handled in small quantities only.

- **Flammability**

1. Flash point: Not applicable

2. Autoignition temperature: Spontaneously flammable at room temperature

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Shut off flow of gas. Carbon dioxide may extinguish the fire, but it will re-ignite spontaneously. If the fire is in a safe location, let the fire burn.

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for phosphine of 0.02 ppm. Although Patty states that the limit of perceptibility is 1.5 to 3.0 ppm, the experience of industrial users confirms the odor threshold given by May.

2. Eye Irritation Level: Grant states that "although numerous instances of poisoning of human beings and experimental animals (from phosphine) have been reported, no characteristic ocular or visual effects are known."

3. Evaluation of Warning Properties: Since the odor of phosphine can be detected at a concentration well below the permissible exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for phosphine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a doping agent in manufacture of solid-state components for electronic circuits and in manufacture of lasers	Local exhaust ventilation; personal protective equipment
Use in preparation of alkyl and aryl phosphonium halides in textile treatment; use in organic intermediates; use as curing catalysts for epoxy resins, polymerization initiators, and condensation catalysts	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a fumigant for stored grain	Local exhaust ventilation; personal protective equipment

Liberation during drilling, machining, and grinding of ductile iron; during quenching of alloys or sludges; during cleaning of rusty metal in phosphoric acid; and during welding of steel coated with phosphate rust-proofing agents	Local exhaust ventilation; personal protective equipment
Liberation during manufacture and use of acetylene; during extraction of phosphorus, and use of inorganic phosphorus compounds use of phosphorus sesquisulfide in manufacture of safety matches and calcium phosphide in pyrotechnics	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of phosphine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If phosphine is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

- Waste disposal method:

Phosphine may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR PHOSPHINE

Condition	Minimum Respiratory Protection* Required Above 0.3 ppm
Gas Concentration	
3 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against phosphine. Any supplied-air respirator. Any self-contained breathing apparatus.
15 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing protection against phosphine. A gas mask with a chin-style or a front- or back-mounted canister providing protection against phosphine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 200 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against phosphine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phosphoric Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H_3PO_4
- Synonyms: White phosphoric acid; ortho-phosphoric acid; 85% phosphoric acid; meta-phosphoric acid
- Appearance and odor: Viscous, colorless, odorless liquid which can solidify at temperatures below 21 C (70 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphoric acid is 1 milligram of phosphoric acid per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphoric acid can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Solid phosphoric acid or its solutions may cause skin burns. Contact with the eyes may produce irritation and eye burns. Exposure to phosphoric acid vapor or mist may cause irritation of the eyes, nose, and throat.

2. Long-term Exposure: Repeated or prolonged exposure may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphoric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphoric acid at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from phosphoric acid exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of phosphoric acid dust or mist might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Phosphoric acid dust, mist, or solutions may cause dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Phosphoric acid mist is an irritant to the eyes, upper respiratory tract, and skin. The solid is especially irritating to skin in the presence of moisture. Unacclimated workers could not endure exposure to fumes of phosphorus pentoxide (the anhydride of phosphoric acid) at a concentration of 100 mg/m^3; exposure to concentrations between 3.6 and 11.3 mg/m^3 produced coughing. Concentrations of 0.8 to 5.4 mg/m^3 were noticeable but not uncomfortable. There is no evidence that phosphorus poisoning can result from contact with phosphoric acid. The risk of pulmonary edema resulting from the inhalation of mist or spray is remote. A dilute solution buffered to pH 2.5 caused a moderate brief stinging sensation but no injury when dropped in the human eye. A 75% solution will cause severe skin burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Boiling point (760 mm Hg): 260 C (500 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of phosphoric acid): 3.4
5. Melting point: 21 C (70 F)
6. Vapor pressure at 20 C (68 F): 0.0285 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong caustics can cause liberation of much heat and violent spattering. Contact with most metals causes formation of flammable and explosive hydrogen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume) may be released when phosphoric acid decomposes.
4. Special precautions: Liquid phosphoric acid will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Phosphoric acid mist can cause irritation of the eyes and respiratory tract, according to the *Hygienic Guide*. No quantitative information is given, however. Deichmann and Gerarde note that since phosphoric acid "has a low vapor pressure at room temperature, it is not irritating to the eyes or respiratory tract, unless introduced into the atmosphere as a spray or mist."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of phosphoric acid on a cellulose membrane filter, followed by leaching with hot water, chemical reaction, and spectrophotometric analysis. An analytical method for phosphoric acid is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid phosphoric acid or solutions containing greater than 1.6% ortho-phosphoric acid by weight or any concentration of meta-phosphoric acid.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing 1.6% or less ortho-phosphoric acid by weight.
- If employees' clothing may have become contaminated with solid phosphoric acid, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with phosphoric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phosphoric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphoric acid, the person performing the operation should be informed of phosphoric acid's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solid or liquid phosphoric acid or solutions containing phosphoric acid, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phosphoric acid should be removed immediately and not reworn until the phosphoric acid is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid phosphoric acid or solutions containing phosphoric acid contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to solid or liquid phosphoric acid or solutions containing more than 1.6% ortho-phosphoric acid by weight, or any concentration of meta-phosphoric acid, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phosphoric acid should be immediately washed or showered to remove any phosphoric acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphoric acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of aluminum products in bright dipping operations; use in cleaning, electropolishing, and pickling in manufacture of steel, brass, bronze, and copper during surface treatment and rust-proofing operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of intermediates in manufacture of soil fertilizers; use in manufacture of livestock and poultry feed	Process enclosure; local exhaust ventilation; personal protective equipment
Use during synthesis of detergent and soap builders and water-treatment chemicals; use as an acidulant and flavor agent in manufacture of carbonated beverages and jellies and preserves	Process enclosure; personal protective equipment
Use in manufacture of food products, intermediates, and food additives; use as an antioxidant and preservative; use in wood, textile, polyurethane foam flame-retardant processing and production of flame-retardant agents	Process enclosure; personal protective equipment
Use in manufacture of cleaning preparations and disinfectants	Process enclosure; personal protective equipment
Use as a bonding agent in manufacture of refractory bricks; use during lithography and photoengraving operations	Process enclosure; personal protective equipment
Use as a catalyst in synthesis of other chemicals; use in synthesis of textile and leather processing chemicals, clays, ceramics, cements, and clay-thinning agents for drilling mud formulations	Process enclosure; personal protective equipment
Use in synthesis of pharmaceuticals and pharmaceutical intermediates and in the extraction of penicillin; use as a laboratory reagent	Process enclosure; personal protective equipment
Use during manufacture of opal glass; during manufacture of dental cements and dentrifice adhesives, adhesive gums, and synthetic rubber; and in the manufacture of electric lights	Process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phosphoric acid gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phosphoric acid gets on the skin, immediately flush the contaminated skin with water. If phosphoric acid soaks through the clothing, remove the clothing immediately and flush the skin with water.

- **Breathing**

If a person breathes in large amounts of phosphoric acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phosphoric acid has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phosphoric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.
3. If in the liquid form, collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Liquid phosphoric acid may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and diposing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Phosphoric Acid," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR PHOSPHORIC ACID

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate or Vapor Concentration	
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phosphorus (Yellow)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: P_4
- Synonyms: White phosphorus; WP; phosphorus, elemental, white
- Appearance and odor: White to yellow, soft, waxy solid which gives off acrid fumes on exposure to air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphorus (yellow) is 0.1 milligram of phosphorus (yellow) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus (yellow) can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: The vapors of burning phosphorus (yellow) are irritating to the nose, throat, and lungs. Severe breathing difficulties may occur. The onset of these difficulties may be delayed for several hours. Phosphorus (yellow) on contact with the skin may ignite and produce severe skin burns with blistering. Phosphorus (yellow) is especially hazardous to the eyes and may produce severe damage. When phosphorus (yellow) is swallowed, after a delay of a few hours, nausea, vomiting, and abdominal pain may occur. The vomit may smell like garlic and glow in the dark. After 24 to 36 hours, the symptoms may go away. In a few hours or 2 or 3 days, the nausea, vomiting, and abdominal pain may reappear with diarrhea and a yellow color to the skin. Death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to phosphorus (yellow) can cause "phossy jaw" with pain and swelling of the jaw, toothaches, loosening of the teeth and destruction of the jawbone. Chronic exposure to phosphorus (yellow) can also cause weakness, anemia, loss of appetite, stomach complaints, cough, and paleness. In addition, chronic exposure to phosphorus (yellow) may cause bones to become brittle and break.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphorus (yellow).

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus (yellow) at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, liver, and kidneys should be stressed. Particular attention should be given to the jaw and teeth. The skin should be examined for evidence of chronic disorders.

—Dental examination: Phosphorus exposure may aggravate existing dental disorders such as caries, periodontal disease, retained roots, and cysts which may predispose to toxic necrosis of the jaw. Dental examination including x-rays should be performed.

—Liver function tests: Since liver damage has been observed in humans exposed to phosphorus, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Complete blood count: Phosphorus exposure may cause anemia. A complete blood count should be per-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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formed including red and white blood cell count, a differential count of a stained blood smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an semi-annual basis.

- **Summary of toxicology**

Yellow phosphorus fume irritates the respiratory tract and eyes; the solid in contact with the skin produces deep thermal burns; prolonged absorption of phosphorus causes necrosis of facial bones. Yellow phosphorus spontaneously burns in air, and the vapors released are irritating to the respiratory tract. The early signs of systemic intoxication by phosphorus are abdominal pain, jaundice, and a garlic odor of the breath; prolonged intake may cause anemia, cachexia, and necrosis of bone, typically the maxilla and mandible. Complaints of possible overexposure among phosphorus workers may be toothache and excessive salivation; there may be dull red appearance of the oral mucosa; one or more teeth may loosen, followed by pain and swelling of the jaw; healing may be delayed following dental procedures such as extractions; with necrosis of bone, sequestra may develop with sinus tract formation. In a series of 10 cases, the shortest period of exposure to phosphorus fume leading to bone necrosis was 10 months (2 cases) and the longest was 18 years. Yellow phosphorus fume causes severe eye irritation with blepharospasm, photophobia, and lacrimation; the solid in the eye produces severe injury. Phosphorus burns on the skin are deep and painful; a firm eschar is produced and is surrounded by vesiculation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 123.9
2. Boiling point (760 mm Hg): 279 C (535 F)
3. Specific gravity (water = 1): 1.82
4. Vapor density (air = 1 at boiling point of phosphorus (yellow)): 4.4
5. Melting point: 44 C (111 F)
6. Vapor pressure at 20 C (68 F): 0.026 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0003
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Light causes formation of yellow or red color.
2. Incompatibilities: Contact with air and all oxidizing agents (including elemental sulfur) will cause fires and explosions. Contact with strong caustics will cause formation of poisonous and flammable phosphine gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume) may be released in a fire involving phosphorus (yellow).
4. Special precautions: Liquid phosphorus (yellow) will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Ignites spontaneously in air at or above 30 C (86 F)
2. Autoignition temperature: 30 C (86 F)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Water, carbon dioxide, sand, warth, dry chemical

- **Warning properties**

Grant states that yellow phosphorus fumes are "irritating to the respiratory tract and cause severe ocular irritation with blepharospasm, photophobia, and lacrimation. Particles of white phosphorus (yellow phosphorus) are caustic and seriously damaging in contact with tissues."

No quantitative information is available concerning the concentrations that produce eye irritation, however.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for phosphorus (yellow) is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use flame-retardant clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid phosphorus (yellow).
- Clothing contaminated with phosphorus (yellow) should be placed underwater in closed containers for storage until it can be discarded or until provision is made for the removal of phosphorus (yellow) from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus (yellow), the person performing the operation should be informed of phosphorus (yellow)'s hazardous properties.
- Where there is any possibility of exposure of an employee's body to solid or liquid phosphorus (yellow), facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes contaminated with phosphorus (yellow) should be removed immediately and not reworn until the phosphorus (yellow) is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid phosphorus (yellow) contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid phosphorus (yellow), an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phosphorus (yellow) should be immediately washed or showered with soap or mild detergent and water to remove any phosphorus (yellow).
- Workers subject to skin contact with solid or liquid phosphorus (yellow) should wash with soap or mild detergent and water any areas of the body which may have contacted phosphorus (yellow) at the end of each work day.
- Eating and smoking should not be permitted in areas where solid or liquid phosphorus (yellow) are handled, processed, or stored.
- Employees who handle solid or liquid phosphorus (yellow) should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphorus (yellow) may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of high purity phosphoric acid salts for use as fertilizers, water treatment chemicals, food products, beverages, and dentrifices; use in synthesis of inorganic phosphorus compounds for use as pesticides, flame retardants for plastics and fibers, and gasoline and lube oil additives; use in synthesis of inorganic and organic compounds	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of phosphorus alloys for introduction into low carbon steel, copper alloys, copper pipe, and bronze	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of explosives, munitions, and pyrotechnics for military use	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst in synthesis of acrylonitrile and organic bromine compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during conversion of yellow phosphorus to red phosphorus for manufacture of wood and paper safety matches	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an ingredient of rat poison and roach powders	Material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phosphorus (yellow) gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phosphorus (yellow) gets on the skin, immediately flush the contaminated skin with water. If phosphorus (yellow) penetrates through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately. The skin should be kept wet until medical attention is obtained to prevent any remaining phosphorus (yellow) from burning.

- **Breathing**

If a person breathes in large amounts of phosphorus (yellow), move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phosphorus (yellow) has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If phosphorus (yellow) is spilled, the following step should be taken:

1. Immediately douse the spill with water and cover with wet sand or dirt.

- Waste disposal method:

Phosphorus (yellow), after solidification and covering with wet sand or dirt, may be disposed of in a secured sanitary landfill.

REFERENCES

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- Summerlin, W. T., et al.: "White Phosphorus Burns and Massive Hemolysis," *Journal of Trauma,* 7:476-484, 1967.

RESPIRATORY PROTECTION FOR PHOSPHORUS (YELLOW)

Condition	**Minimum Respiratory Protection*** **Required Above 0.1 mg/m³**
Particulate Concentration	
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phosphorus Pentachloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: PCl_5
- Synonyms: None
- Appearance and odor: Pale yellow solid with an odor like hydrochloric acid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphorus pentachloride is 1 milligram of phosphorus pentachloride per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus pentachloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to phosphorus pentachloride may cause irritation of the eyes and respiratory tract. Cases of bronchitis have resulted from exposure to this chemical. Severe breathing difficulties may occur. These breathing difficulties may be delayed in onset several hours after exposure has ceased. Phosphorus pentachloride on the skin may cause burning and irritation of the skin.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphorus pentachloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus pentachloride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, skin, and eyes should be stressed.

—14" x 17" chest roentgenogram: Phosphorus pentachloride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Phosphorus pentachloride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Phosphorus pentachloride fume is a severe irritant of the eyes and mucous membranes. Exposure of mice to 120 ppm for 10 minutes was fatal. In humans, the fume causes irritation of the eyes and respiratory tract, and cases of bronchitis have resulted from exposure; although not reported, delayed onset of pulmonary edema may occur. The material on the skin could be expected to cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 167 C (333 F) (sublimes)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of phos-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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phorus pentachloride): Not applicable (reacts rapidly with water in air)

5. Melting point: 167 C (333F) (sublimes)
6. Vapor pressure at 20 C (68 F): Less than 1
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts to form hydrogen chloride and phosphoric acid
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause containers to burst. Exposure to moisture will cause the development of pressure in closed containers.

2. Incompatibilities: Contact with water will cause violent spattering and formation of toxic hydrogen chloride gas and phosphoric acid mist. Phosphorus pentachloride reacts with magnesium oxide, chemically active metals such as sodium and potassium, and with alkalies.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosphoric acid mist, and carbon monoxide) may be released in a fire involving phosphorus pentachloride.

4. Special precautions: Phosphorus pentachloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Patty states that phosphorus pentachloride "has a pungent, unpleasant odor." No quantitative information is available concerning the odor threshold, however.

2. Irritation Levels: Patty states that the "vapor or fume is very irritant to all mucous membranes, including the lungs." No quantitative information is available concerning the threshold of eye irritation, however.

3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for phosphorus pentachloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with phosphorus pentachloride or liquids containing phosphorus pentachloride.
- If employees' clothing may have become contaminated with solid phosphorus pentachloride, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with phosphorus pentachloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phosphorus pentachloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus pentachloride, the person performing the operation should be informed of phosphorus pentachloride's hazardous properties.
- Where there is any possibility of exposure of an employee's body to phosphorus pentachloride or liquids containing phosphorus pentachloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phosphorus pentachloride should be removed immediately and not reworn until the phosphorus pentachloride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of phosphorus pentachloride or liquids containing phosphorus pentachloride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to phosphorus pentachloride or liquids

containing phosphorus pentachloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phosphorus pentachloride should be immediately washed or showered to remove any phosphorus pentachloride.
- Eating and smoking should not be permitted in areas where solid phosphorus pentachloride is handled, processed, or stored.
- Employees who handle phosphorus pentachloride or liquids containing phosphorus pentachloride should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphorus pentachloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chlorinating agent in organic synthesis or chemical reactant for aryl or alkyl acids and salts, ketones, aldehydes, and synthesis of phosphorus compounds	Local exhaust ventilation; personal protective equipment
Use as a catalyst in organic synthesis in production of polyethylene from ethylene	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phosphorus pentachloride or liquids containing phosphorus pentachloride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If phosphorus pentachloride or liquids containing phosphorus pentachloride get on the skin, immediately flush the contaminated skin with water. If phosphorus pentachloride or liquids containing phosphorus pentachloride penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention.

- **Breathing**

If a person breathes in large amounts of phosphorus pentachloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If phosphorus pentachloride or liquids containing phosphorus pentachloride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the phosphorus pentachloride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If phosphorus pentachloride is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill, or
3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with small spray of water, then excess water, and dispose in a secured sanitary landfill.

- Waste disposal method:

See 2 and 3 above.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Phosphorus Pentachloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR PHOSPHORUS PENTACHLORIDE

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate or Vapor Concentration	
10 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and/or gases and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phosphorus Pentasulfide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: P_2S_5 or P_4S_{10}
- Synonyms: Phosphorus persulfide; regular phosphorus pentasulfide; reactive phosphorus pentasulfide; distilled phosphorus pentasulfide; undistilled phosphorus pentasulfide
- Appearance and odor: Greenish-yellow solid with the odor of rotten eggs.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphorus pentasulfide is 1 milligram of phosphorus pentasulfide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus pentasulfide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Phosphorus pentasulfide on contact with water (including the water normally found in air) may produce hydrogen sulfide. This is a primary health hazard associated with phosphorus pentasulfide. Hydrogen sulfide is a very dangerous chemical. It smells like rotten eggs, but at high concentrations paralyzes the sense of smell so that the odor will not be noticed. Hydrogen sulfide acts as an irritant to the eyes and respiratory tract and can produce severe breathing difficulties which may not occur until a number of hours after exposure has ceased. High concentrations of hydrogen sulfide can stop breathing immediately and cause death. Phosphorus pentasulfide, if allowed to remain on the skin, may cause irritation. On contact with the eyes, it may cause serious irritation which may be delayed for a matter of hours.

2. *Long-term Exposure:* Repeated exposure to hydrogen sulfide released from contact of water with phosphorus pentasulfide will increase a person's sensitivity to hydrogen sulfide so that irritation of the eyes, coughing, dizziness, headache, and tiredness and other systemic effects may occur more readily.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphorus pentasulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus pentasulfide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, central nervous system, eyes, and skin should be stressed.

—14" x 17" chest roentgenogram: Phosphorus pentasulfide in contact with water will release hydrogen sulfide, which causes respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Phosphorus pentasulfide in contact with water will release hydrogen sulfide, which causes respiratory impairment. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when

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indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Phosphorus pentasulfide dust irritates the eyes and skin. Since it is readily converted in the presence of moisture to hydrogen sulfide gas and phosphoric acid, its inhalation toxicology is based on hydrogen sulfide. The latter is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations; it is an irritant of the eyes and respiratory tract at low concentrations. Inhalation of high concentrations of hydrogen sulfide, 1000 to 2000 ppm, may cause coma after a single breath and may be rapidly fatal; convulsions may also occur. Exposure to concentrations of hydrogen sulfide above 50 ppm for 1 hour may produce acute conjunctivitis with pain, lacrimation, and photophobia; in severe form this may progress to keratoconjunctivitis and vesiculation of the corneal epithelium. In low concentrations, hydrogen sulfide may cause headache, fatigue, irritability, insomnia, and gastrointestinal disturbances; in somewhat higher concentrations, it affects the central nervous system, causing excitement and dizziness. Prolonged exposure to 250 ppm may cause pulmonary edema. Prolonged exposure to concentrations as low as 50 ppm may cause rhinitis, pharyngitis, bronchitis, and pneumonitis. Repeated exposure to hydrogen sulfide results in increased susceptibility, so that eye irritation, cough, and systemic effects may result from concentrations previously tolerated without any effect. Rapid olfactory fatigue can occur at high concentrations.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.3 (or 444.6)
2. Boiling point (760 mm Hg): 513 C (955 F)
3. Specific gravity (water = 1): Bulk density powder = 1.3; solid = 2.1; liquid = 1.7
4. Vapor density (air = 1 at boiling point of phosphorus pentasulfide): Not applicable
5. Melting point: 275 C (527 F)
6. Vapor pressure at 300 C (572 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts to form hydrogen sulfide and liberate heat
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, particularly in presence of moisture or moist air
2. Incompatibilities: Contact with water, alcohols, and strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, hydrogen sulfide, phosphorus pentoxide, phosphoric acid fume, and carbon monoxide) may be released in a fire involving phosphorus pentasulfide.
4. Special precautions: None listed

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: 260 – 290 C (500 – 544 F) (dust); 275 C (527 F) (liquid) (approximately)
3. Minimum explosive concentration: Data not available
4. Extinguishant: Dry chemical, carbon dioxide, dry sand for small fires

- **Warning properties**

1. Odor Threshold: The MCA states that phosphorus pentasulfide reacts with moisture to liberate hydrogen sulfide. Phosphorus pentasulfide, according to the MCA, has a "characteristic hydrogen sulfide odor."
2. Eye Irritation Level: Phosphorus pentasulfide itself is not a known eye irritant. Hydrogen sulfide, however, which is liberated when the compound comes into contact with atmospheric moisture, is known to produce eye (and respiratory) irritation after 1 hour at 50 to 100 ppm (MCA).
3. Evaluation of Warning Properties: Since hydrogen sulfide "paralyzes" olfactory nerves at high concentrations "and, therefore, cannot be detected by odor," phosphorus pentasulfide is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for phosphorus pentasulfide had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforce-

ment and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with phosphorus pentasulfide or liquids containing phosphorus pentasulfide.
- If employees' clothing may have become contaminated with solid phosphorus pentasulfide, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with phosphorus pentasulfide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phosphorus pentasulfide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus pentasulfide, the person performing the operation should be informed of phosphorus pentasulfide's hazardous properties.
- Non-impervious clothing which becomes contaminated with phosphorus pentasulfide should be removed promptly and not reworn until the phosphorus pentasulfide is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where phosphorus pentasulfide or liquids containing phosphorus pentasulfide may contact the eyes.

SANITATION

- Skin that becomes contaminated with phosphorus pentasulfide should be promptly washed or showered with soap or mild detergent and water to remove any phosphorus pentasulfide.
- Eating and smoking should not be permitted in areas where solid phosphorus pentasulfide is handled, processed, or stored.
- Employees who handle phosphorus pentasulfide or liquids containing phosphorus pentasulfide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphorus pentasulfide may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of lubrication oil additives for low-lead gas and reduction of air pollution	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phosphorus pentasulfide or liquids containing phosphorus pentasulfide get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid phosphorus pentasulfide gets on the skin, dust it off immediately and then flush the contaminated skin with water. If phosphorus pentasulfide or liquids containing phosphorus pentasulfide penetrate through the clothing, remove the clothing promptly and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of phosphorus pentasulfide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phosphorus pentasulfide or liquids containing phosphorus pentasulfide have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If phosphorus pentasulfide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and

burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device, or

3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with small spray of water, then excess water, and dispose in a secured sanitary landfill.

- Waste disposal methods:

Phosphorus pentasulfide may be disposed of:

1. By making packages of phosphorus pentasulfide in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving phosphorus pentasulfide in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. See 2 and 3 above.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Phosphorus Pentasulfide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR PHOSPHORUS PENTASULFIDE

Condition	**Minimum Respiratory Protection* Required Above 1 mg/m³**
Particulate Concentration	
10 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
750 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 750 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen sulfide and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phosphorus Trichloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: PCl_3
- Synonyms: Phosphorus chloride
- Appearance and odor: Colorless to yellow fuming liquid with an odor like hydrochloric acid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphorus trichloride is 0.5 part of phosphorus trichloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3 milligrams of phosphorus trichloride per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for phosphorus trichloride from 0.5 ppm to 0.2 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus trichloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Phosphorus trichloride is a severe irritant of the eyes, mucous membranes, and skin and may produce severe burns. Inhalation of the vapor may cause irritation of the respiratory tract. It may produce severe breathing difficulties which may be delayed as much as a day in onset. Phosphorus trichloride on contact with the eyes may produce severe burns with permanent eye damage. Swallowing phosphorus trichloride may produce burns of the mouth, throat, and stomach.

2. Long-term Exposure: Repeated inhalation of phosphorus trichloride may cause chronic cough and wheezing.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphorus trichloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus trichloride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, skin, eyes, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Phosphorus trichloride causes lung damage in humans. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Phosphorus trichloride causes delayed pulmonary edema. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Phosphorus trichloride vapor is a severe irritant of the eyes, mucous membranes, and skin. These effects result primarily from the action of the strong acids, hydrochloric acid and acids of phosphorus, formed with water. In rats, the LC50 was 104 ppm for 4 hours; at autopsy, the chief finding was nephrosis; pulmonary

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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damage was negligible. Inhalation by humans could be expected to cause injury ranging from mild bronchial spasm to severe pulmonary edema; the onset of severe respiratory symptoms may be delayed for 2 to 6 hours, and after moderate exposure the onset may not occur until 12 to 24 hours later. Prolonged or repeated exposure to low concentrations may induce chronic cough and wheezing; pulmonary changes are non-fibrotic and non-progressive. Phosphorus trichloride causes severe burns in contact with the eyes, skin, or mucous membranes. Although ingestion is unlikely to occur in industrial use, it will cause burns of the mouth, throat, esophagus, and stomach.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 137.4
2. Boiling point (760 mm Hg): 75.9 C (168 F)
3. Specific gravity (water = 1): 1.57
4. Vapor density (air = 1 at boiling point of phosphorus trichloride): 4.75
5. Melting point: −112 C (−169 F)
6. Vapor pressure at 20 C (68 F): 100 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts violently to form hydrogen chloride
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat may cause containers to burst. Containers may burst if water enters them.
2. Incompatibilities: Contact with water or alcohol may cause fires and explosions, particularly when in contact with combustible organic matter. Phosphorus trichloride reacts with chemically active metals such as sodium, potassium, and aluminum or with strong nitric acid.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosphine, diphosphine, phosphoric acid, and carbon monoxide) may be released when phosphorus trichloride decomposes.
4. Special precautions: Phosphorus trichloride will attack some forms of plastics, rubber, and coatings. In the presence of moisture, phosphorus trichloride will severely corrode most metals.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold. The MCA notes that this substance has a pungent odor.
2. Eye Irritation Level: Grant states that "experimentally in cats a concentration of 2 to 4 ppm in air in the course of 6 hours has caused conjunctivitis."
3. Other Information: Grant points out that the vapors are irritating to the respiratory tract also. The *Documentation of TLV's* states that a concentration of 0.7 ppm "was somewhat irritating to animals."
4. Evaluation of Warning Properties: Since phosphorus trichloride causes irritation at only 0.7 ppm, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for phosphorus trichloride had been published by NIOSH.

- **Method**

An analytical method for phosphorus trichloride is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

can be discarded or until provision is made for the removal of phosphorus trichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus trichloride, the person performing the operation should be informed of phosphorus trichloride's hazardous properties.

- Where there is any possibility of exposure of an employee's body to liquid phosphorus trichloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phosphorus trichloride should be removed immediately and not reworn until the phosphorus trichloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid phosphorus trichloride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid phosphorus trichloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phosphorus trichloride should be immediately washed or showered to remove any phosphorus trichloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphorus trichloride may occur and control methods which may be effective in each case:

Operation	Controls
Use during synthesis of plasticizers and intermediates; and production of intermediates and during chemical synthesis of dyes, pharmaceuticals, other chlorinating agents, and other organic chemicals	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of pesticide intermediates and surfactants	Process enclosure; local exhaust ventilation; personal protective equipment
Use during deposition of metallic coatings; use in treatment of polypropylene before drying in manufacture of knitted fabrics	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid phosphorus trichloride or strong concentrations of phosphorus trichloride vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid phosphorus trichloride gets on the skin, immediately flush the contaminated skin with water. If liquid phosphorus trichloride soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of phosphorus trichloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid phosphorus trichloride has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the phosphorus trichloride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid phosphorus trichloride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material, or;
3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with a small spray of water, then excess water, and dispose in a secured sanitary landfill.

- Waste disposal method:

Phosphorus trichloride may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill or as in 3 above.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Phosphorus Trichloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Baskin, A. D. (ed.): *Handling Guide for Potentially Hazardous Commodities,* Railway Systems and Management Association, Chicago, 1972.
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- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals,* Academic Press, New York, 1969.
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- Patty, F. A. (ed.): *Toxicology,* Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Weeks, M. H., et al.: "Acute Vapor Toxicity of Phosphorus Oxychloride, Phosphorus Trichloride and Methyl Phosphonic Dichloride," *American Industrial Hygiene Association Journal,* 25:470-475, 1964.

RESPIRATORY PROTECTION FOR PHOSPHORUS TRICHLORIDE

Condition	Minimum Respiratory Protection* Required Above 0.5 ppm
Vapor Concentration	
25 ppm or less	Any chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxidizable sorbents and providing protection against phosphorus trichloride. A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against phosphorus trichloride Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 50 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-oxidizable sorbents and providing protection against phosphorus trichloride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Phthalic Anhydride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_4(CO)_2O$
- Synonyms: PAN
- Appearance and odor: White solid with a characteristic choking odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phthalic anhydride is 2 parts of phthalic anhydride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of phthalic anhydride per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for phthalic anhydride a Threshold Limit Value of 1 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phthalic anhydride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Phthalic anhydride causes irritation of the eyes, nose, throat, and skin. The irritant effects are worse on moist surfaces. If phthalic anhydride is held in contact with the skin as under clothes or shoes, skin burns may occur. Inhalation of the dust or vapors may cause coughing, sneezing, or nosebleeds. Inhalation may cause attacks of asthma in persons who have previously had asthma.

2. Long-term Exposure: Repeated or prolonged exposure to phthalic anhydride may cause a skin rash or chronic eye irritation. Repeated exposures may also cause an allergic type of skin rash. It may cause bronchitis and asthma.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phthalic anhydride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phthalic anhydride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to phthalic anhydride would be expected to be at increased risk from exposure. Examination of the eyes, respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Phthalic anhydride in the form of vapor, fume, or dust irritates the eyes; it is both an irritant and sensitizer of the skin and respiratory tract, and may produce asthma on repeated exposure. Cats repeatedly exposed to 3700 mg/m^3 became drowsy, lost appetite and vomited; liver and kidney injury occurred. In workers, air concentrations of 30 mg/m^3 caused conjunctivitis; at 25 mg/m^3 there were signs of mucous membrane irritation. Workers exposed to undetermined concentrations of mixed vapors of phthalic acid and phthalic anhydride developed conjunctivitis, bloody nasal discharge, atrophy of the nasal mucosa, hoarseness, cough, occasional bloody

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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sputum, and bronchitis. A report of emphysema among workers exposed to phthalic anhydride is questionable. Several cases of bronchial asthma resulted; there was skin sensitization with occasional urticaria and eczematous response. Phthalic anhydride is a direct but delayed irritant of the skin; it is more severely irritating in contact with water, due to the pronounced effects of the phthalic acid which is formed. Prolonged or repeated exposure also may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 148
2. Boiling point (760 mm Hg): 284 C (543 F)
3. Specific gravity (water = 1): 1.5
4. Vapor density (air = 1 at boiling point of phthalic anhydride): 5.1
5. Melting point: 131 C (268 F)
6. Vapor pressure at 20 C (68 F): Less than 0.05 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.62 (reacts slowly)
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as phthalic acid fumes and carbon monoxide) may be released in a fire involving phthalic anhydride.
4. Special precautions: Liquid phthalic anhydride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 151 C (304 F) (closed cup)
2. Autoignition temperature: 570 C (1058 F)
3. Flammable limits in air, % by volume (at elevated temperatures): Lower: 1.7; Upper: 10.4
4. Minimum explosive dust concentration: 0.015 g/l
5. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

According to both Patty and the *Hygienic Guide*, exposure to a concentration of 30 mg/m^3 causes "definite conjunctival irritation." This concentration is not stated specifically to be the threshold of eye irritation, however.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of phthalic anhydride on a cellulose membrane filter, followed by treatment with aqueous ammonia, hydrolysis, and anlysis with a high-performance liquid chromatograph. An analytical method for phthalic anhydride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid phthalic anhydride or liquids containing phthalic anhydride.
- If employees' clothing may have become contaminated with solid phthalic anhydride, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with phthalic anhydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phthalic anhydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phthalic anhydride, the person performing the operation should be informed of phthalic anhydride's hazardous properties.

- Non-impervious clothing which becomes contaminated with phthalic anhydride should be removed immediately and not reworn until the phthalic anhydride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid phthalic anhydride or liquids containing phthalic anhydride may contact the eyes.

SANITATION

- Skin that becomes contaminated with phthalic anhydride should be immediately washed or showered with soap or mild detergent and water to remove any phthalic anhydride.
- Employees who handle solid phthalic anhydride or liquids containing phthalic anhydride should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phthalic anhydride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of plasticizers for use in polyvinyl chloride, polyvinyl acetate, copolymer resins, cellulosic plastics, alkyd resins, and nondrying oils or natural resins to enhance properties; manufacture of unsaturated polyester resins for use in structural building parts, swimming pools, automotive parts, and luggage	Process enclosure; general dilution ventilation
Use in synthesis of dyes; use in manufacture of chemicals and chemical intermediates for production of insecticides, insect repellants, chemical reagents, urethane polymers, perfumes, and weed killers	Process enclosure; general dilution ventilation; personal protective equipment
Use in manufacture of pharmaceuticals and pharmaceutical intermediates; manufacture of metallic and acid salts; manufacture of epoxy resins as curing and hardening agents	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of fire retardants for use as components of polyester resins	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If phthalic anhydride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid phthalic anhydride or liquids containing phthalic anhydride get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid phthalic anhydride or liquids containing phthalic anhydride penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of phthalic anhydride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When phthalic anhydride has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If phthalic anhydride is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid containing phthalic anhydride should be absorbed in vermiculite, dry sand, earth, or a similar material for disposal in a secured sanitary landfill.

- Waste disposal methods:

Phthalic anhydride may be disposed of:

1. By making packages of phthalic anhydride in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving phthalic anhydride in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. Liquid containing phthalic anhydride should be absorbed in vermiculite, dry sand, earth, or a similar material and deposited in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Phthalic Anhydride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-61, Phthalic Anhydride*, Washington, D.C., 1956.
- National Institute for Occupational Safety and Health: "Hazard Entry No. 161 — Phthalic Anhydride," *Hazard Process Index*.
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- Shick, D., and Glick, D. (eds.): *Methods of Biochemical Analysis*, Vol. 32, Interscience, New York, 1974.

RESPIRATORY PROTECTION FOR PHTHALIC ANHYDRIDE

Condition	**Minimum Respiratory Protection*** **Required Above 2 ppm**
Particulate or Vapor Concentration	
100 ppm or 600 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1670 ppm or 10,000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1670 ppm or 10,000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Picric Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HOC_6H_2(NO_2)_3$
- Synonyms: 2,4,6-Trinitrophenol; lyddite; pertite; shimose; melinite
- Appearance and odor: Odorless yellow solid or paste.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for picric acid is 0.1 milligram of picric acid per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Picric acid can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed.

- **Effects of overexposure**

Exposure to picric acid dust and fume may cause eye and skin irritation. The dust and solutions of picric acid may cause an allergic skin rash. The skin and hair may be stained yellow. Inhalation of high concentrations of dust has caused unconsciousness, weakness, muscle pain, and kidney problems. Swallowing picric acid may cause a bitter taste, headache, dizziness, nausea, vomiting, and diarrhea. High doses may cause destruction of the red blood cells and damage to the kidneys and liver with blood in the urine. High doses such as these may color the skin and other tissues yellow and cause yellow tinted vision.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to picric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to picric acid at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to picric acid may be at increased risk from exposure. Examination of the kidneys, liver, and blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to picric acid, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to picric acid, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Picric acid dust causes sensitization dermatitis. This usually occurs on the face, especially around the mouth and the sides of the nose; the condition progresses from edema, through the formation of papules and vesicles, to ultimate desquamation. The skin and hair of workers handling picric acid are stained yellow. Inhalation of high concentrations of the dust by one worker caused temporary coma followed by weakness, myalgia, anuria, and later polyuria. Following ingestion of 2 to 5 g of picric acid, which has a bitter taste, there may be

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headache, vertigo, nausea, vomiting, diarrhea, yellow coloration of the skin, hematuria, and albuminuria; high doses cause destruction of erythrocytes, hemorrhagic nephritis, and hepatitis. High doses which cause systemic intoxication will color all tissues yellow, including the conjunctiva and aqueous humor, and cause apparent yellow-tinted vision. Corneal injury has resulted from a splash of a solution of picric acid into the eyes; dust or fume may cause eye irritation which may be aggravated by sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 229.1
2. Boiling point (760 mm Hg): Greater than 300 C (572 F); explodes
3. Specific gravity (water = 1): 1.6 – 1.76
4. Vapor density (air = 1 at boiling point of picric acid): Not applicable
5. Melting point: 122 C (252 F)
6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.4
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Explodes above 300 C (572 F)
2. Incompatibilities: Contact with copper, lead, zinc, and other metals (or with their salts) can form salts of picric acid that are initiators and much more sensitive to shock than picric acid itself. Shock-sensitive salts also include ammonium salts and calcium salts; the calcium salt may form when picric acid comes into contact with plaster or concrete.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving picric acid.
4. Special precautions: Protect from shock.

- **Flammability**

1. Flash point: 150 C (302 F) (closed cup)
2. Autoignition temperature: 300 C (572 F) (approx).
3. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): 82 cm
4. Explosion temperature (temperature required to cause explosion in 5 seconds): 322 C (612 F)
5. Flammable limits in air, % by volume: Data not available
6. Extinguishant: Water. Do not attempt to extinguish massive fires.

- **Warning properties**

The ILO states, "The effects of picric acid on the eyes include irritation, corneal injury and strange visual effects, e.g. yellow appearance of objects, and yellow colouring of the tissues." Grant also states that "picric acid dust or fumes cause irritation of the eyes of men and animals, and this may be aggravated by sensitization." No quantitative information is available concerning the air concentrations which produce these effects, however. Information is not available concerning the threshold of eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure picric acid may be used. An analytical method for picric acid is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent skin contact with solid picric acid or liquids containing picric acid, where skin contact may occur.

- If employees' clothing may have become contaminated with picric acid, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which may have become contaminated with picric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of picric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the picric acid, the person performing the operation should be informed of picric acid's hazardous properties.
- Non-impervious clothing which becomes contaminated with picric acid should be removed promptly and not reworn until the picric acid is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid picric acid or liquids containing picric acid may contact the eyes.

SANITATION

- Workers subject to skin contact with solid picric acid or liquids containing picric acid should wash any areas of the body which may have contacted picric acid at the end of each work day.
- Skin that becomes contaminated with picric acid should be promptly washed or showered with soap or mild detergent and water to remove any picric acid.
- Eating and smoking should not be permitted in areas where solid picric acid or liquids containing picric acid is handled, processed, or stored.
- Employees who handle solid picric acid or liquids containing picric acid should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to picric acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in munitions and explosives manufacturing	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of dyes and dye intermediates in textile industry; use in manufacture of medicinals; use in etching of metal on printing plates of copper, steel, or other metals	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of pyrotechnics and compounds for pyrotechnics as color intensifiers and as an oxidizer in matches	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use as a chemical reagent in identification, isolation, and purification of other compounds; use in manufacture of colored glass; and in the manufacture of electric batteries	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If picric acid or liquids containing picric acid get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If picric acid or liquids containing picric acid get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If picric acid or liquids containing picric acid penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of picric acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When picric acid or liquids containing picric acid have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If picric acid is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. Attempt to reclaim spilled material; however, do not sweep or burn unless this is supervised by explosive experts.

- Waste disposal method:

Picric acid may be disposed of only by explosives experts.

ADDITIONAL INFORMATION

To find additional information on picric acid, look up picric acid in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR PICRIC ACID

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
1 mg/m³ or less	Any dust and mist respirator, except single-use respirator or quarter-mask.** Any fume respirator or high efficiency particulate filter respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Pival

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{14}H_{14}O_3$
- Synonyms: 2-Pivalyl-1,3-indandione; pivalyl; tert-butyl-valone; 2-pivaloyl-1,3-indandione; 1,3-dioxo-2-pivaloy-lindane; pindone
- Appearance and odor: The technical material, which is a 0.5% concentrate in an inert solid, is a bright yellow solid with almost no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Pival is 0.1 milligram of Pival per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pival may be absorbed by swallowing, or indirectly by inhalation, and is probably not significantly absorbed through the skin.

- **Effects of overexposure**

Pival causes no immediate symptoms. Swallowing Pival, particularly in repeated smaller doses, may cause generalized bleeding, such as nose bleeds, excessive bleeding of minor cuts, smoky urine, or black, tarry stools. A person may experience stomach and back pain one to several days after being exposed to Pival.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Pival.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Pival at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination, including a complete blood count: The effects of overexposure from Pival can be enhanced or mimicked in individuals who have blood disorders with bleeding tendencies or with diseases that cause internal bleeding, such as peptic ulcer. Also, those with chronic liver disease may be increased risk, as are those on therapeutic doses of anticoagulants.

—Prothrombin time: The principal action of Pival is to reduce the level of prothrombin, prolonging the prothrombin time. This test is critical to the monitoring of exposed employees.

2. *Periodic Medical Examination:* At three months from the first exposure and annually thereafter, the employer should make available to the employee medical procedures listed under the preplacement examination. Also, if an employee develops signs or symptoms associated with Pival exposure at any time during employment, the employer should provide medical examinations to the employee.

- **Summary of toxicology**

Pival is a vitamin K antagonist, inhibiting prothrombin formation. Since repeated doses have a cumulative effect, a toxic concentration may be reached after several days of exposure to small doses. In rats, the ingestion of a single large dose of Pival causes rapid death due to pulmonary and visceral congestion without hemorrhage and may not be related to vitamin K antagonism. Death in animals from chronic exposure is due to multiple internal hemorrhage.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 230
  2. Boiling point (760 mm Hg): Data not available

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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3. Specific gravity (water = 1): 1.06

4. Vapor density (air = 1 at boiling point of Pival): Data not available

5. Melting point: 110 C (230 F)

6. Vapor pressure at 20 C (68 F): Data not available

7. Solubility in water, g/100 g water at 20 C (68 F): 0.0018

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Very high temperatures
2. Incompatibilities: None known
3. Hazardous decomposition products: None known
4. Special precautions: None known

- **Flammability**

1. Not flammable

- **Warning properties**

Pival is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air sampies should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for Pival had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- If employees' clothing may have become contaminated with Pival, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with Pival should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of Pival from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the Pival, the person performing the operation should be informed of Pival's hazardous properties.

SANITATION

- Eating and smoking should not be permitted in areas where Pival is handled, processed, or stored.
- Employees who handle Pival should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Pival may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mixing and packaging operations in pesticide formulations	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area
Liberation during mixing and blending of pesticide formulation with other materials (cereal bait, liquid, etc).	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area
Liberation during synthesis of substance; during use as an intermediate in pharmaceutical synthesis	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area
Liberation during container reclamation, process clean-up, etc.	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If Pival gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Swallowing**

When Pival has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Pival is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Pival may be disposed of:

1. By making packages of Pival in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving Pival in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR PIVAL

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use respirators.
1 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. Any high efficiency particulate filter respirator with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use respirators. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Platinum Salts (as Platinum)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble platinum salts (as platinum). Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Sodium chloroplatinate

- Formula: $Na_2PtCl_6\text{-}6H_2O$
- Synonyms: None
- Appearance and odor: Yellow-orange, odorless solid.

Ammonium chloroplatinate

- Formula: $(NH_4)_2PtCl_6$
- Synonyms: Ammonium hexachloroplatinate
- Appearance: Yellow-orange solid.

Platinum tetrachloride

- Formula: $PtCl_4$
- Synonyms: Platinum (IV) chloride
- Appearance: Brown-red crystals.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble platinum salts is 0.002 milligram of soluble platinum salts (as platinum) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble platinum salts can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble platinum salts may cause irritation of the eyes, nose, and throat.

2. Long-term Exposure: Repeated exposure to soluble platinum salts may cause both respiratory and skin allergies. The respiratory reaction starts with sneezing and a runny nose. These effects may be followed by chest tightness, shortness of breath, blue discoloration of the skin, and wheezing. The skin reaction consists of an itchy red rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble platinum salts.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble platinum salts at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to soluble platinum salts would be expected to be at increased risk from exposure. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Soluble platinum salts in the form of dusts and sprays cause asthma, skin sensitization, and eye irritation; elemental platinum does not produce these effects.

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Workers repeatedly exposed to platinum salts in concentrations of from 2 to 20 ug/m^3 of workroom air developed irritation of the nose and upper respiratory tract with sneezing and running of the eyes, leading to cough, chest tightness, asthmatic wheezing with dyspnea and cyanosis, which became progressively more severe with further exposure. A relative lymphocytosis is commonly present. Skin exposure results in contact dermatitis with pruritis and urticaria; an eczematous eruption often results. Some exposed individuals experience both dermal and respiratory effects due to sensitization; the majority of individuals exposed repeatedly to platinum salts develop some allergic symptoms. Removal from platinum salt exposure results in almost immediate relief of asthma; the dermatitis usually clears in 1 to 2 days but may be persistent. In the eyes, the dusts cause a burning sensation, lacrimation, and conjunctival hypermia sometimes associated with photophobia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Sodium chloroplatinate**

1. Molecular weight: 561.9
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.5
4. Vapor density (air = 1 at boiling point of soluble platinum salts): Not applicable
5. Melting point: Loses water at 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 50
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Ammonium chloroplatinate**

1. Molecular weight: 443.9
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 3.1
4. Vapor density (air = 1 at boiling point of soluble platinum salts): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.7
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Platinum tetrachloride**

1. Molecular weight: 336.9
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.3
4. Vapor density (air = 1 at boiling point of soluble platinum salts): Not applicable
5. Melting point: Decomposes at 370 C (698 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 25 C (77 F): 58.7
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause formation of poisonous chlorine gas.
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine) may be released when chlorine-containing soluble platinum salts decompose.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Grant reports that "the dusts of soluble platinum salts cause a burning sensation in the eyes, lacrimation, and conjunctival hyperemia, sometimes associated with photophobia, which suggests that the corneal epithelium may be involved." However, no quantitative information concerning the concentrations of the dusts which produce these symptoms is given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of soluble platinum salts on a filter, followed by treatment with nitric and perchloric acids, solution in acid, and atomic absorption analysis. An analytical method for soluble platinum salts is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).
(order number PB 265 029).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforce-

ment and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with soluble platinum salts or liquids containing soluble platinum salts, where skin contact may occur.
- If employees' clothing may have become contaminated with soluble platinum salts or liquids containing soluble platinum salts, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with soluble platinum salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of soluble platinum salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the soluble platinum salts, the person performing the operation should be informed of soluble platinum salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with soluble platinum salts should be removed promptly and not reworn until the soluble platinum salts are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble platinum salts or liquids containing soluble platinum salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with soluble platinum salts should be promptly washed or showered to remove any soluble platinum salts.
- Eating and smoking should not be permitted in areas where soluble platinum salts or liquids containing soluble platinum salts are handled, processed, or stored.
- Employees who handle soluble platinum salts or liquids containing soluble platinum salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble platinum salts may occur and control methods which may be effective in each case:

Operation	Controls
Use as catalysts in production of high octane gasoline; nitric and sulfuric acids; vinyl esters, petrochemicals, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use and re-use in reclamation of platinum ore; use in electroplating industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in photographic and related industries as a photographic paper sensitizer	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If soluble platinum salts or liquids containing soluble platinum salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If soluble platinum salts or liquids containing soluble platinum salts get on the skin, promptly flush the contaminated skin with water. If soluble platinum salts or liquids containing soluble platinum salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble platinum salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble platinum salts or liquids containing soluble platinum salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Under-

stand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble platinum salts or liquids containing soluble platinum salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble platinum salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble platinum salts may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOLUBLE PLATINUM SALTS (AS PLATINUM)

Condition	**Minimum Respiratory Protection*** **Required Above 0.002 mg/m³**
Particulate Concentration	
0.1 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
4 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 4 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PORTLAND CEMENT

INTRODUCTION

This guideline summarizes pertinent information about Portland cement (containing less than 1 percent quartz) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Varies with composition of specific cement

- **Synonyms**

Hydraulic cement, Portland cement silicate, cement

- **Identifiers**

1. CAS No.: 65997-15-1
2. RTECS No.: VV8770000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Portland cement is a finely divided gray powder containing less than 1 percent silica and composed of lime, alumina, silica, and iron oxide; small amounts of magnesia, sodium, potassium, and sulfur are also present. This substance is odorless.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: Varies with specific cement
2. Boiling point: Not applicable
3. Specific gravity: Not reported
4. Vapor density: Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Insoluble in water
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: None reported
3. Hazardous decomposition products: None reported
4. Special precautions: None reported.

- **Flammability**

The National Fire Protection Association has not

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assigned a fire hazard rating for Portland cement; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving Portland cement should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving Portland cement.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for Portland cement is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hour time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned Portland cement a threshold limit value (TLV) of 10 mg/m3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of physical irritation associated with exposure to Portland cement [NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to Portland cement can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Instilled intratracheally, cement dust caused an absorptive reaction in guinea pig lungs. Peritoneal nodules formed initially and then decreased progressively in size and eventually resolved spontaneously [ACGIH 1991].
2. *Effects on Humans:* Portland cement dust causes eye irritation, and prolonged or repeated contact of the dust or cement with the skin causes dermatitis [Hathaway et al. 1991]. Fifteen of 95 cement workers studied had a mild dermatitis of the hands [Hathaway et al. 1991]. A study of 2,736 Portland cement workers revealed that 5.4 percent of these workers had dyspnea, compared with a 2.7 percent prevalence among controls. There were no differences in mean pulmonary function test results between the two groups [Hathaway et al. 1991]. The mean cement dust exposure for these workers was 0.57 mg/m^3 (respirable dust), with peaks to 46 mg/m3 [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to Portland cement include physical irritation of the eyes, with redness and tearing; coughing; and redness, roughness, and scaling of the skin.
2. *Chronic exposure:* The signs and symptoms of repeated or prolonged exposure of the skin to Portland cement include coughing, expectoration, exertional dyspnea, and skin redness, blistering, burns, and, in some individuals, raised itching areas characteristic of hives.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of Portland cement is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve Portland cement and lead to worker exposures to this substance:

—Use as a binding agent in concrete and mortar

The following methods are effective in controlling worker exposures to Portland cement, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to Portland cement, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to Portland cement at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to Portland cement exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of Portland cement on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for Portland cement.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne Portland cement is made using a tared low ash polyvinyl chloride (LAPVC) filter, 5 microns, preceded by a 10-mm nylon cyclone. A maximum air volume of 960 liters is collected at a maximum flow rate of 2 liters/min. A gravimetric analysis is then performed to measure compliance with the respirable Portland cement standard. Following this determination, an x-ray diffraction analysis of respirable quartz is done to determine compliance with the quartz standard. These methods are described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985a], *NIOSH Occupational Exposure Sampling Strategy Manual* [NIOSH 1977] and Method No. ID-142 of the *OSHA Analytical Methods Manual* [OSHA 1985b].

PERSONAL HYGIENE

If Portland cement dust contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with Portland cement dust should be removed, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of Portland cement, particularly its potential to cause dermatitis on prolonged contact.

A worker who handles Portland cement should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where Portland cement is handled, processed, or stored.

STORAGE

Portland cement should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of Portland cement should be protected from physical damage.

SPILLS

In the event of a spill involving Portland cement, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.

2. Notify safety personnel.

3. Avoid creating dust during cleanup by using a vacuum or a wet method for cleanup.

4. For dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Portland cement is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.30] to notify the National Response Center of an accidental release of Portland cement; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of Portland cement emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although Portland cement is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of Portland cement exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, and gauntlets) should be worn to prevent prolonged skin contact with Portland cement. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to Portland cement permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to Portland cement.

Safety glasses, goggles, or face shields should be worn during operations in which Portland cement might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with Portland cement. Contact lenses should not be worn if the potential exists for Portland cement exposure.

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Occupational Health Guideline for Cyanide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all cyanides. Physical and chemical properties of two specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Potassium cyanide

- Formula: KCN
- Synonyms: None
- Appearance and odor: White solid with a faint almond odor.

Sodium cyanide

- Formula: NaCN
- Synonyms: None
- Appearance and odor: White solid with a faint almond odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyanide is 5 milligrams of cyanide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 5 milligrams cyanide per cubic meter of air averaged over a 10-minute period. The NIOSH Criteria Document for Hydrogen Cyanide and Cyanide Salts should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyanide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. Sufficient cyanide may be absorbed through the skin, especially if there are cuts to cause fatal poisoning.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation or ingestion of cyanide salts may be rapidly fatal. Larger doses by inhalation or swallowing may cause the person to rapidly lose consciousness, stop breathing, and die. In some cases, there are convulsions. At lower levels of exposure, the earlier symptoms include weakness, headache, confusion, nausea, and vomiting. These symptoms may be followed by unconsciousness and death. Occasionally, convulsions occur. Milder forms of intoxication may result only in weakness, dizziness, headache, and nausea. The dust of cyanide salts is irritating to the eyes. In the presence of tears, it may cause the symptoms of poisoning described above. The dust of cyanide salts may produce irritation of the nose and skin. Strong solutions of cyanide salts are corrosive and may produce ulcers.

2. Long-term Exposure: Effects from chronic exposure to cyanide are non-specific and rare.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyanide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyanide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of fainting spells, such as occur in various types of cardiovascular and nervous disorders,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and those unusually susceptible to effects of anoxia or with anemia would be expected to be at increased risk from exposure. Examination of the cardiovascular, nervous, and upper respiratory systems, and thyroid should be stressed. The skin should be examined for evidence of chronic disorders.

—Skin disease: Cyanide is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—14" x 17" chest roentgenogram: Cyanide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Cyanide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

3. *First Aid Kits:* First aid kits should be readily available in workplaces where there is a potential for the release of cyanide. These kits should contain a minimum of 48 ampules, each of 0.3 ml amyl nitrate, and complete instructions for use. In addition, 2 physician's kits should be immediately available to trained medical personnel. These kits should contain the above quantity of amyl nitrate as well as sterile sodium nitrite solution (3%) and sterile sodium thiosulfate solution (25%). All of the above drugs should be replaced at least biannually to ensure their potency.

- **Summary of toxicology**

The dust of cyanide salts, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. Cyanide exerts this effect because it inactivates certain enzymes by forming very stable complexes with the metal in them. Cytochrome oxidase is probably the most important of these, since it occupies a fundamental position in the respiratory process and is involved in the ultimate electron transfer to molecular oxygen. Since cytochrome oxidase is present in practically all cells that function under aerobic conditions, and since the cyanide ion diffuses easily to all parts of the body, it is capable of suddenly bringing to a halt practically all cellular respiration. In the presence of even weak acids, hydrocyanic acid (HCN) gas is liberated from cyanide salts; a few inhalations of higher concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, 135 ppm after 30 minutes, and 110 ppm may be fatal in 1 hour. The ingestion by humans of 50 to 100 mg of sodium or potassium cyanide may also be fatal. At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth is usually increased initially and at later stages becomes slow and gasping; if cyanosis is present, it usually indicates that respiration has either ceased or has been very inadequate for a few minutes. Humans tolerate 45 to 54 ppm for ½ to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours. Sodium cyanide dust is irritating to the eyes; in the presence of tears it may liberate HCN, which can be absorbed and cause systemic intoxication. Skin contact with dust may be irritating; strong solutions on the skin produce ulcers which are slow in healing. Cyanide is one of the few toxic materials for which an antidote exists; it functions as follows: First, amyl nitrite (inhalation) and sodium nitrite (intravenously) are administered to form methemoglobin, which binds firmly with free cyanide ions. This traps any circulating cyanide ions. The formation of 10 to 20% methemoglobin usually does not involve appreciable risk, yet provides a large amount of cyanide-binding substance. Second, sodium thiosulfate is administered intravenously to increase the rate of conversion of cyanide to the less toxic thiocyanate. Methylene blue should not be administered, because it is a poor methemoglobin former and, moreover, promotes the conversion of methemoglobin back to hemoglobin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Potassium cyanide**

1. Molecular weight: 65.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.55
4. Vapor density (air = 1 at boiling point of potassium cyanide): Not applicable
5. Melting point: 635 C (1175 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 71.6
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Sodium cyanide**

1. Molecular weight: 49
2. Boiling point (760 mm Hg): 1500 C (2732 F) (extrapolated)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of sodium cyanide): Not applicable
5. Melting point: 560 C (1040 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 58
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None. Hazardous if kept in closed containers. It may form toxic concentrations of hydrogen cyanide gas when in prolonged contact with air in a closed area.
2. Incompatibilities: Contact with strong oxidizers such as nitrates and chlorates may cause fires and

explosions. Contact with acids and acid salts causes immediate formation of toxic and flammable hydrogen cyanide gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide and carbon monoxide) may be released when cyanide decomposes.

4. Special precautions: Cyanide may react with carbon dioxide in ordinary air to form toxic hydrogen cyanide gas.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of sodium or potassium cyanide. HCN, however, is evolved from these substances in the presence of moisture. The Manufacturing Chemists Association states that "although HCN has a characteristic odor, its toxic action at hazardous concentrations is so rapid that it is of no value as a warning property."

2. Eye Irritation Level: Cyanide (as CN) is not known to be an eye irritant. However, according to Grant, HCN can produce eye irritation after chronic exposures.

3. Evaluation of Warning Properties: Although cyanide (as CN) has a negligible vapor pressure, in the presence of moisture HCN can be given off. HCN does not have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cyanide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of cyanide with a cellulose membrane filter and an impinger containing sodium hydroxide, followed by analysis by direct potentiometry. An analytical method for cyanide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with cyanide or liquids containing cyanide.
- If employees' clothing has had any possibility of being contaminated with cyanide, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with cyanide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyanide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyanide, the person performing the operation should be informed of cyanide's hazardous properties.
- Where there is any possibility of exposure of an employee's body to cyanide or liquids containing cyanide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with cyanide should be removed immediately and not reworn until the cyanide is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of cyanide or liquids containing cyanide contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to cyanide or liquids containing cyanide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with cyanide should be immediately washed or showered with soap or mild detergent and water to remove any cyanide.
- Workers subject to skin contact with cyanide should wash with soap or mild detergent and water any areas of the body which may have contacted cyanide at the end of each work day.
- Eating and smoking should not be permitted in areas where cyanide or liquids containing cyanide are handled, processed, or stored.
- Employees who handle cyanide or liquids containing cyanide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyanide may occur and control methods which may be effective in each case:

Operation	Controls
Use as fumigants and pesticides in greenhouses, ships, mills, and warehouses; use of cyanogen chloride as a warning agent in fumigant gases	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metal treatment in nitriding, tempering, and case hardening steel; coloring of metals by chemical or electrolytic process; cleaning and coating metals; welding and cutting of heat-resistant metals; liberation during ore extraction and metal purification	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use of calcium cyanamid in fertilizer on soil; during chemical synthesis for manufacture of intermediates in pharmaceuticals, dyes, vitamins, plastics, and sequestering agents; preparation of nitriles, carbylamines, cyano fatty acids, and inorganic cyanides	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cellulose technology; paper manufacture; in dyeing; as cement stabilizers; use in photography as fixatives, and in blueprinting and process engraving; liberation in blast furance gases or in handling of illuminating gas	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If cyanide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with cyanides.

- **Skin Exposure**

If cyanide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If cyanide penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of cyanide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When cyanide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If cyanide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation, or for treatment in a cyanide disposal system.

- Waste disposal method:

After treatment as in above, cyanide may be disposed of in a secured sanitary landfill.

REFERENCES

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- von Oettingen, W. F.: *Poisoning: A Guide to Clinical Diagnosis and Treatment* (2nd ed.), Saunders, Philadelphia, 1958.
- Wolfsie, J. H.: "Treatment of Cyanide Poisoning in Industry," *A.M.A. Archives of Industrial Hygiene and Occupational Medicine*, 4:417-425, 1951.

RESPIRATORY PROTECTION FOR CYANIDE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen cyanide and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Propane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH_2CH_3$
- Synonyms: Dimethylmethane
- Appearance and odor: Colorless, odorless gas (a foul-smelling odorant is usually added).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propane is 1000 parts of propane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of propane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propane can affect the body if it is inhaled.

- **Effects of overexposure**

Overexposure to propane may cause dizziness, disorientation, and excitation. Greater exposure may cause unconsciousness and death. Contact with liquefied propane may cause a freezing injury or frostbite.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propane.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to propane at potentially hazardous levels.

- **Summary of toxicology**

Propane, a gas at ordinary temperatures, is an asphyxiant in very high concentrations. Guinea pigs exposed to concentrations of up to 5.5% propane by volume (55,000 ppm) for 1 to 2 hours showed tremors after 5 minutes, then nausea, retching and stupefaction; all survived and at autopsy had no significant tissue damage. Brief exposures to 10,000 ppm caused no symptoms in human subjects; 100,000 ppm produced slight dizziness in a few minutes of exposure but was not noticeably irritating to the eyes, nose, or respiratory tract. In the very few reports of accidental overexposure, there was disorientation, excitation, excessive salivation, headache, and vomiting. Liquid propane may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44.1
2. Boiling point (760 mm Hg): −42.1 C (−43.7 F)
3. Specific gravity (water = 1): 0.5 (liquid)
4. Vapor density (air = 1 at boiling point of propane): 1.6
5. Melting point: −187.7 C (−305.8 F)
6. Vapor pressure at 20 C (68 F): 8.6 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving propane.
4. Special precautions: Liquid propane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (gas)

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Autoignition temperature: 450 C (842 F)

3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 9.5

4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: Patty reports that the odor threshold of propane is 20,000 ppm.

2. Irritation Levels: According to Patty, exposure to concentrations as high as 100,000 ppm "is not noticeably irritating to the eyes, nose, or respiratory tract."

3. Evaluation of Warning Properties: Propane has poor warning properties. The odor threshold is 20 times the permissible exposure limit, and no noticeable irritation is produced at a concentration 100 times the permissible exposure limit.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by utilizing a combustible gas meter. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure propane may be used. An analytical method for propane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid propane or from contact with vessels containing liquid propane.
- Any clothing which becomes wet with liquid propane should be removed immediately and not reworn until the propane has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid propane may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to propane may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from use as a component of liquid petroleum gas for commercial and industrial usage	General dilution ventilation
Use as feedstock in cracking process in production of ethylene and propylene and motor gasoline with high antiknock properties and stability	Process enclosure; general dilution ventilation
Use as a basic material in chemical synthesis for oxidation, alkylation, nitration, and chlorination	Process enclosure; general dilution ventilation
Use as a solvent and extractant in deasphalting and degreasing of crude oils in production of lubricating oils, refining of fish and vegetable oils, extraction of oils from agricultural products, and segregate of specialty oils	Process enclosure; general dilution ventilation

Use as a refrigerant in chemical, petroleum refining, and gas processing operations, low-temperature crystallizers, and helium recovery from natural gas	Process enclosure; general dilution ventilation
Use as a fuel in welding and cutting operations; use in high-grade metallurgical work in which sulfur-free fuel is essential	General dilution ventilation
Use in oil wells to increase production of crude oil	Process enclosure
Use in desalination of water; use in hydrocarbon-fueled cells as source of power (experimental)	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquefied propane gets into the eyes, flush eyes immediately with large amounts of water. Do not use hot water for eye flushing. Get medical attention immediately.

- **Skin Exposure**

If liquefied propane gets on the skin, immediately flush the contaminated skin with water. If liquefied propane soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of propane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If propane is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

- Waste disposal method:

Propane may be disposed of by burning at a safe location or in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Propane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Underwriters' Laboratories: *Propane*.

RESPIRATORY PROTECTION FOR PROPANE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
20,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR beta-PROPIOLACTONE

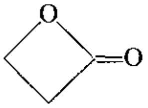
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about beta-propiolactone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_3H_4O_2$
- **Structure:**



- **Synonyms:** 2-Oxetanone; BPL; hydracrylic acid beta-lactone; 3-hydroxypropionic acid lactone; propanolide; 1,3-propiolactone; 3-propiolactone; beta-propionolactone.
- **Identifiers:** CAS 57-57-8; RTECS RQ7350000; DOT not assigned
- **Appearance and odor:** Colorless liquid with a pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72.06
2. Boiling point (at 760 mmHg): 162 °C (323.6 °F), decomposes
3. Specific gravity (water = 1): 1.1460
4. Vapor density (air = 1 at boiling point of beta-propiolactone): 2.5
5. Melting point: -33.4°C (-28.12 °F)
6. Vapor pressure at 25 °C (77 °F): 3.4 mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): 37
8. Evaporation rate (butyl acetate = 1): 0.223
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 0.45% (4,473 ppm)

- **Reactivity**

1. Incompatibilities: beta-Propiolactone polymerizes during storage, hydrolyzes readily in water, and decomposes if stored at room temperature.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving beta-propiolactone.
3. Caution: beta-Propiolactone can polymerize and rupture containers, especially at elevated temperatures.

- **Flammability**

1. Flash point: 74°C (165 °F) (closed cup)
2. Flammable limits in air, % by volume: Lower, 2.9; upper, not available
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for beta-propiolactone; however, the OSHA standard requires implementation of stringent controls wherever beta-propiolactone or solid or liquid mixtures containing at least 0.1% by weight or volume of beta-propiolactone are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1013, beta-Propiolactone. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated beta-propiolactone as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 0.5 parts of beta-propiolactone per million parts of air (ppm) [1.5 milligrams per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration for a normal 8-hour workday or a 40-hour workweek.

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HEALTH HAZARD INFORMATION

- **Routes of exposure**

beta-Propiolactone may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

Effects on animals: In rats, acute oral administration or intraperitoneal injection of beta-propiolactone caused muscular spasms, respiratory difficulty, convulsions, and death. Acute intravenous injection caused kidney tubule and liver damage. Subcutaneous injection of beta-propiolactone in rats and mice produced cancer at the sites of administration. Single intraperitoneal injections in suckling mice produced lymphatic tumors and liver cancer.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to beta-propiolactone can cause irritation and blistering of the skin, hair loss, and scarring. Eye contact with liquid beta-propiolactone can cause permanent corneal opacification.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to beta-propiolactone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys and respiratory systems. Medical surveillance for respiratory diseases should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to beta-propiolactone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic diseases of the skin or liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to beta-propiolactone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, eyes, liver, kidneys, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to beta-propiolactone may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

There are no NIOSH-validated sampling and analytical methods for beta-propiolactone.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where beta-propiolactone is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where beta-propiolactone is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in the designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with beta-propiolactone should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of beta-propiolactone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beta-propiolactone's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove beta-propiolactone from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1013:

Areas where beta-propiolactone is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of beta-propiolactone, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving beta-propiolactone which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of beta-propiolactone into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where beta-propiolactone is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of beta-propiolactone shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove beta-propiolactone from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to beta-propiolactone may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for beta-propiolactone

Operations	Controls
During use in the manufacture of acrylic acids and esters; during use in the sterilization of blood plasma, tissue grafts, and surgical instruments; during use in research and laboratory facilities	Process enclosure, restricted access, local exhaust ventilation where appropriate, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures If a worker had contact with beta-propiolactone, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to beta-propiolactone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If beta-propiolactone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to beta-propiolactone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If beta-propiolactone gets on the skin, wash it immediately with soap and water. If beta-propiolactone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter aras of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If beta-propiolactone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing beta-propiolactone should be absorbed on paper towels and placed in an appropriate container.
4. Large quantities of liquids containing beta-propiolactone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing beta-propiolactone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: When engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for beta-propiolactone

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for n-Propyl Acetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3COOCH_2CH_2CH_3$
- Synonyms: Propyl acetate; acetic acid n-propyl ester
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for n-propyl acetate is 200 parts of n-propyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 840 milligrams of n-propyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Propyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to n-propyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to n-propyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to n-propyl acetate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from n-propyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of n-propyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: n-Propyl acetate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although n-propyl acetate is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although n-propyl acetate is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The toxicologic effects of n-propyl acetate are chiefly irritation of the conjunctiva and upper respiratory tract, followed by narcosis. Cats exposed to 5300 ppm for 6 hours daily showed eye irritation and salivation; at 24,500 ppm there was narcosis and death. No chronic systemic effects have been reported in humans.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102
2. Boiling point (760 mm Hg): 101.6 C (215 F)
3. Specific gravity (water = 1): 0.89
4. Vapor density (air = 1 at boiling point of n-propyl acetate): 3.5
5. Melting point: −95 C (−140 F)
6. Vapor pressure at 20 C (68 F): 25 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 2
8. Evaporation rate (butyl acetate = 1): 2.75

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving n-propyl acetate.
4. Special precautions: n-Propyl acetate will dissolve many plastics and resins.

- **Flammability**

1. Flash point: 14 C (58 F) (closed cup)
2. Autoignition temperature: 450 C (842 F)
3. Flammable limits in air, % by volume: Lower: 2; Upper: 8
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

1. Odor Threshold: According to the *Handbook of Organic Industrial Solvents,* the odor of n-propyl acetate is detectable at the permissible exposure limit.
2. Eye Irritation Level: The *Handbook of Organic Industrial Solvents* states that n-propyl acetate "causes irritation of mucous membranes at the threshold limit."
3. Evaluation of Warning Properties: Through its odor and irritant effects, n-propyl acetate can be detected at the TLV. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of n-propyl acetate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure n-propyl acetate may be used. An analytical method for n-propyl acetate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid n-propyl acetate.
- Clothing wet with liquid n-propyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of n-propyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the n-propyl acetate, the person performing the operation should be informed of n-propyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid n-propyl acetate should be removed immediately and not reworn until the n-propyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid n-propyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid n-propyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any n-propyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to n-propyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use in spray, brush, or dip application of lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during application of adhesives; manufacture of lacquers and adhesives	Local exhaust ventilation; general dilution ventilation
Use as a solvent for rubber; during application of solvent for plastics, nitrocellulose, and cellulosic derivatives and resins; during brush or dip applications of lacquers; during preparation of flavoring agents and perfumes	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If n-propyl acetate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If n-propyl acetate gets on the skin, promptly flush the contaminated skin with water. If n-propyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of n-propyl acetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When n-propyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the affected person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If n-propyl acetate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. n-Propyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

n-Propyl acetate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR N-PROPYL ACETATE

Condition	**Minimum Respiratory Protection* Required Above 200 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
8000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Propyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH_2CH_2OH$
- Synonyms: n-Propyl alcohol; 1-propanol; ethyl carbinol
- Appearance and odor: Colorless liquid with a mild, non-residual, alcoholic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propyl alcohol is 200 parts of propyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 500 milligrams of propyl alcohol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to high air concentrations of propyl alcohol may cause mild irritation of the eyes, nose, and throat. Drowsiness, headaches, and incoordination may also occur. Swallowing propyl alcohol may cause drowsiness, unconsciousness, and death. Gastrointestinal pain, cramps, nausea, vomiting, and diarrhea may also result from swallowing this alcohol.

2. Long-term Exposure: Prolonged skin exposure may cause drying and cracking of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to propyl alcohol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from propyl alcohol exposure.

—Skin disease: Propyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although propyl alcohol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although propyl alcohol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of propyl alcohol might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The principal action of propyl alcohol is that of a mild narcotic, but it may also act as an upper respiratory tract irritant. Mice exposed to vapor developed ataxia in 90 to 120 minutes at 3250 ppm; deep narcosis occurred after 240 minutes' exposure at 4100 ppm. Propyl alcohol is absorbed, oxidized, and eliminated more rapidly than

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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is ethyl alcohol. Skin absorption has been demonstrated in animals, as well as mild irritation of the skin on repeated exposure due to defatting action. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60
2. Boiling point (760 mm Hg): 97 C (207 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of propyl alcohol): 2.1
5. Melting point: −126 C (−195 F)
6. Vapor pressure at 20 C (68 F): 15 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 1.3

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving propyl alcohol.
4. Special precautions: Propyl alcohol will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 15 C (59 F) (closed cup)
2. Autoignition temperature: 440 C (824 F)
3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 13.5
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Summer and May report odor thresholds of 30 ppm.
2. Eye Irritation Level: n-Propyl alcohol, according to Grant, resembles "ethyl alcohol in physical and toxic properties." Grant states that a vapor concentration of 2500 ppm has "no notable effect on the eyes." The AIHA *Hygienic Guide* notes that above 5500 ppm, some eye and nasal irritation occur.
3. Evaluation of Warning Properties: Since the odor threshold of n-propyl alcohol is below the permissible exposure limit (200 ppm), it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of propyl alcohol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure propyl alcohol may be used. An analytical method for propyl alcohol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

number PB 246 148).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid propyl alcohol.
- Clothing wet with liquid propyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of propyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propyl alcohol, the person performing the operation should be informed of propyl alcohol's hazardous properties.
- Any clothing which becomes wet with liquid propyl alcohol should be removed immediately and not reworn until the propyl alcohol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid propyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid propyl alcohol should be promptly washed or showered to remove any propyl alcohol.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to propyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Liberation and use during spray application of surface coatings containing solvent, polystyrene coatings, and dopes	Local exhaust ventilation; personal protective equipment
Liberation during use as a chemical intermediate in organic synthesis	Local exhaust ventilation; general dilution ventilation
Use during printing on plastic film and sheeting with polyamide-based inks	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during textile and leather processing	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in application of surface coatings other than spray or heat in nitrocellulose lacquers, dopes, and polystyrene coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture and packaging of surface coatings as a solvent in nitrocellulose lacquers, dopes, polystryrene coatings, inks, dyes, textiles, leather finishes, and artists' fixatives; manufacture of cleaning preparations and polishing agents	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in extraction of vegetable oils, castor oil, and pharmaceuticals; use during cleaning and degreasing operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during cellulose processing; spinning of acrylonitrile; manufacture of brake fluids	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If propyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If propyl alcohol gets on the skin, flush the contaminated skin with water. If propyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of propyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When propyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If propyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Propyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Propyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Propyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR PROPYL ALCOHOL

Condition	**Minimum Respiratory Protection* Required Above 200 ppm**
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Propylene Dichloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CHClCH_2Cl$
- Synonyms: 1,2-Dichloropropane
- Appearance and odor: Colorless liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene dichloride is 75 parts of propylene dichloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 350 milligrams of propylene dichloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propylene dichloride can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to propylene dichloride causes eye and skin irritation and may cause drowsiness or lightheadedness.
2. *Long-term Exposure:* Prolonged overexposure to propylene dichloride may affect the liver and kidneys.
3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propylene dichloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to propylene dichloride at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from propylene dichloride exposure.

—Skin disease: Propylene dichloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Propylene dichloride is known as a liver toxin in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Propylene dichloride is known as a kidney toxin in animals and justifies special consideration before exposing persons with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of propylene dichloride might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Propylene dichloride vapor is a narcotic and an eye irritant. At 2200 ppm for 7 hours, guinea pigs developed severe conjunctival swelling, as well as signs of respiratory irritation and incoordination; some died after 5 daily exposures, showing severe liver injury, some kidney injury, and occasional adrenal changes. Repeated inhalation of 1000 ppm caused some deaths among dogs after 24 exposures of 7 hours' duration, and among rats after only 7 exposures. There was early onset of lacrimation, eye irritation, and incoordination. Liver damage was the main finding in the animals that died. At 400 ppm, rats and guinea pigs exposed for up to 140

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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daily 7-hour exposures showed no ill effects and no histologic changes. However, of a group of C3H-strain mice exposed at 400 ppm, some died; others developed hepatomas, a finding of equivocal significance. Propylene dichloride is mildly irritating to human skin, and some skin absorption may occur from exposure to the liquid. The undiluted liquid is moderately irritating to the eyes but does not cause permanent injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 113
2. Boiling point (760 mm Hg): 96.1 C (205 F)
3. Specific gravity (water = 1): 1.16
4. Vapor density (air = 1 at boiling point of propylene dichloride): 3.9
5. Melting point: −100 C (−148 F)
6. Vapor pressure at 20 C (68 F): 39.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.26
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Strong acids may cause decomposition.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and hydrogen chloride) may be released in a fire involving propylene dichloride.
4. Special precautions: Propylene dichloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 15.6 C (60 F) (closed cup)
2. Autoignition temperature: 557 C (1035 F)
3. Flammable limits in air, % by volume (at 100 C): Lower: 3.4; Upper: 14.5
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold of 50 ppm. The AIHA *Hygienic Guide* states that "human subjects described the odor as 'strong' at 130 to 190 ppm and 'not noticeable' at 15 to 23 ppm."
2. Eye Irritation Level: According to Grant, "exposure of guinea pigs to 2200 ppm in air for many hours until most were dead caused lacrimation and swelling of the lids and conjunctiva. To the extent that the corneas were left unprotected, bluish discoloration of the corneas and infection developed. Rabbits exposed to the same conditions showed little irritation." No quantitative information is available concerning the threshold of eye irritation. No ill effects have been observed in animals chronically exposed to 400 ppm.
3. Evaluation of Warning Properties: Since the odor threshold of propylene dichloride is below the permissible exposure limit, this substance is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of propylene dichloride vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure propylene dichloride may be used. An analytical method for propylene dichloride is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).
PB 265 026).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid propylene dichloride.
- Clothing wet with liquid propylene dichloride should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of propylene dichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene dichloride, the person performing the operation should be informed of propylene dichloride's hazardous properties.

- Any clothing which becomes wet with liquid propylene dichloride should be removed immediately and not reworn until the propylene dichloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid propylene dichloride may contact the eyes.

SANITATION

- Skin that becomes wet with liquid propylene dichloride should be promptly washed or showered with soap or mild detergent and water to remove any propylene dichloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to propylene dichloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a soil fumigant for protection of fruit and nut crops, field crops, beets, and tobacco against nemotodes	Adequate ventilation; personal protective equipment
Use in cleaning, degreasing, and spot removal operations including paint and varnish removal	Local exhaust ventilation; personal protective equipment
Use during rubber compouding and vulcanizing operations	Local exhaust ventilation; personal protective equipment
Use during extraction processing of fats, oils, lactic acid, and petroleum waxes	Local exhaust ventilation; personal protective equipment
Use in the manufacture of tetrachloroethylene and propylene oxide	Local exhaust ventilation; personal protective equipment
Use as an additive and lead scavenger in antiknock fluids	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If propylene dichloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If propylene dichloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If propylene dichloride soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of propylene dichloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When propylene dichloride has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If propylene dichloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Propylene dichloride should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Propylene dichloride may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Propylene Dichloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.

RESPIRATORY PROTECTION FOR PROPYLENE DICHLORIDE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
400 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Propylene Imine*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_3H_7N
- Synonyms: 2-Methylaziridine
- Appearance and odor: Fuming, colorless liquid with a strong, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene imine is 2 parts of propylene imine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of propylene imine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propylene imine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to propylene imine causes eye irritation.

2. Long-term Exposure: Repeated doses fed to animals have been shown to cause cancer.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propylene imine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to propylene imine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, breasts, eyes, nervous system, and blood should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Propylene imine has been shown to cause granulocytic leukemia in rats repeatedly exposed to oral doses as little as 10 mg/kg. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Propylene imine vapor is a carcinogen in animals. This compound has also caused eye irritation. Exposure of rats to 500 ppm for 4 hours was fatal, but inhalation for 2 hours resulted in no deaths. Rats given 20 mg/kg by gavage twice weekly suffered from advanced flaccid paralysis after 18 weeks, and the mortality rate was high; at 10 mg/kg, paralysis occurred to a lesser extent after 30 weeks; granulocytic leukemia, squamous cell carcinoma of the ear duct, and brain tumors (glioma) were observed in different animals; females showed mammary adenocarcinomas, a number of which metastasized to the lung. When placed in the eye of a rabbit, a 5% aqueous solution produced corneal damage; it is also said to have caused injury to human eyes, but details have not been provided.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 57
2. Boiling point (760 mm Hg): 66 C (151 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of propylene imine): 2
5. Melting point: −65 C (−85 F)
6. Vapor pressure at 20 C (68 F): Data not available
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat; contact with acids
2. Incompatibilities: Contact with acids will cause violent polymerization that may burst containers. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving propylene imine.
4. Special precautions: Liquid propylene imine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −4 C (25 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: The ILO reports that "no industrial injuries (from propylene imine) have been reported, other than severe eye burns." According to Grant, the liquid "has caused severe damage when applied to rabbit eyes, similar in severity to 28% ammonium hydroxide." Patty reports that propylene imine causes acute effects which are similar to those caused by ethylene imine. Among the acute effects produced by ethylene imine are eye, nose, and throat irritation. For the purposes of this guideline, therefore, propylene imine is treated as an eye irritant.
3. Evaluation of Warning Properties: Since there are no available quantitative data relating the warning properties of propylene imine to air concentrations, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for propylene imine had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid propylene imine, where skin contact may occur.
- Clothing contaminated with propylene imine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of propylene imine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene imine, the person performing the operation should be informed of propylene imine's hazardous properties.
- Where exposure of an employee's body to liquid propylene imine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with propylene imine or non-impervious clothing which becomes contaminated with propylene imine should be removed immediately and not reworn until the propylene imine is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid propylene imine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid propylene imine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with propylene imine should be immediately washed or showered to remove any propylene imine.
- Eating and smoking should not be permitted in areas where liquid propylene imine is handled, processed, or stored.
- Employees who handle liquid propylene imine should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to propylene imine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a polymer modifier to improve physical properties of polymer; to improve wet adhesion, brushability and freeze-to-thaw stability of paints, improve shrink-proofing agents of woolen textiles, and improve electrical properties of wire-coating materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of polypropylene imines and polymers for coating materials, adhesives, chelating agents, emulsifying agents, and fire-proofing agents in textile, rubber, paint, ink, and paper industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in pharmaceutical and chemical industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If propylene imine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If propylene imine gets on the skin, immediately flush the contaminated skin with water. If propylene imine soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of propylene imine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When propylene imine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If propylene imine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Dilute with water spray until no longer flammable. Add 4% acetic acid (vinegar) solution to the diluted spill until vinegar odor of acid is present, and flush the diluted and neutralized spill. Liquid propylene imine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal and neutralization methods:

Propylene imine may be disposed of:

1. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. If larger quantities, by diluting with water, then adding acetic acid in excess of that required to neutralize the propylene imine.

ADDITIONAL INFORMATION

To find additional information on propylene imine, look up propylene imine in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Propylene Imine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR PROPYLENE IMINE

Condition	**Minimum Respiratory Protection* Required Above 2 ppm**
Vapor Concentration	
100 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against propylene imine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Propylene Oxide *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3CHOCH_2
- Synonyms: 1,2-Epoxypropane; propene oxide; methyloxirane
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene oxide is 100 parts of propylene oxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 240 milligrams of propylene oxide per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for propylene oxide from 100 ppm to 20 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propylene oxide can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to propylene oxide may cause irritation of the eyes, nose, throat, and lungs. Contact with propylene oxide liquid may cause skin or eye irritation or burns.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propylene oxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to propylene oxide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from propylene oxide exposure.

—Skin disease: Propylene oxide can cause dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although propylene oxide is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although propylene oxide is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of propylene oxide might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Propylene oxide is a severe irritant and a mild depressant of the central nervous system. Excessive exposure of animals to vapors caused irritation of the eyes, upper respiratory tract, and lungs, as well as central nervous system effects characterized by ataxia, incoordination, and general depression. The LC50 for single exposures of rats was 3600 ppm, while 400 to 500 ppm was lethal

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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to some rats on repeated daily exposures. The predominant effect was lung irritation and infection. All animals tolerated repeated exposures of 100 ppm without effects. Reported adverse effects on man have been confined to injury to the eyes, and skin. The vapor is irritating to the eyes and the liquid causes corneal burns. When confined to the skin, as from wearing contaminated clothing or shoes, the material and water solutions as dilute as 10% are likely to cause irritation, blistering, and even burns upon single, short exposures. Some evidence indicates that solutions more dilute than 10% may be more irritating than the undiluted propylene oxide. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58
2. Boiling point (760 mm Hg): 34 C (94 F)
3. Specific gravity (water = 1): 0.83
4. Vapor density (air = 1 at boiling point of propylene oxide): 2.0
5. Melting point: −112 C (−170 F)
6. Vapor pressure at 20 C (68 F): 442 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 40.5
8. Evaporation rate (butyl acetate = 1): 33.7

- **Reactivity**

1. Conditions contributing to instability: Heat; contact with acids and caustics
2. Incompatibilities: Anhydrous metal chlorides such as iron or aluminum chloride, strong acids, caustics, and peroxides cause polymerization with liberation of heat.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving propylene oxide.
4. Special precautions: Propylene oxide will attack some forms of plastics, rubber, and coatings. No acetylide-forming metals such as copper or copper alloys should be in contact with propylene oxide.

- **Flammability**

1. Flash point: −37 C (−35 F) (closed cup)
2. Autoignition temperature: 748 C (1378 F)
3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 37.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that "the median detectable concentration of propylene oxide vapors is reported to be 200 ppm with 95% confidence limits of 114 to 353 ppm. The odor is described as sweet, alcoholic, and like natural gas, ether, or benzene."
2. Eye Irritation Level: Grant reports that "exposure of monkeys and rabbits to 457 ppm of vapor in air for 7 hours daily had no adverse effect, but in rats and guinea pigs it irritated the eyes and induced lung edema."

The AIHA *Hygienic Guide*, Patty, the *Documentation of TLV's*, and several other sources all note that propylene oxide causes eye irritation. However, no quantitative information is available, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Patty states that "neither odor nor irritation can be relied upon to warn of the presence of vapor concentrations not suitable for prolonged and repeated exposure. Odor and/or irritation will warn of the presence of acutely dangerous concentrations." Since it appears that Patty considers any vapor concentrations above 100 ppm (the ACGIH threshold limit for 1961) "not suitable for prolonged and repeated exposure," propylene oxide is considered to have adequate warning properties for the purposes of this guideline. The median of the detectable odor concentrations (200 ppm) is only twice the permissible exposure limit. The chronic exposure data given in the *Documentation of TLV's* quoted below do not indicate that 200 ppm causes any toxic effects.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of propylene oxide vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure propylene oxide may be used. An analytical method for propylene oxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid propylene oxide.
- Clothing wet with liquid propylene oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of propylene oxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene oxide, the person performing the operation should be informed of propylene oxide's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid propylene oxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid propylene oxide or any clothing which becomes wet with liquid propylene oxide should be removed immediately and such clothing should not be reworn until the propylene oxide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid propylene oxide may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid propylene oxide should be immediately washed or showered to remove any propylene oxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to propylene oxide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of polypropylene glycol and polyether polyols in production of polyurethane foam; manufacture of propylene glycol for use as a solvent, emulsifier, and mold inhibitor; manufacture of dipropylene glycol for use as a solvent, ink formulations, and glycol esters for solvents, oil additives, and hydraulic brake fluids	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in the production of lubricants, surfactants, and miscellaneous chemicals for pharmaceutical, petroleum, textile, rubber, and soap industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a low-boiling solvent for cellulose derivatives, hydrocarbons, commercial gums, and various resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a fumigant (moth-proofing agent), herbicide, germicide, insecticide, and stabilizer of vinyl resin lacquers and discoloration preventer of hydrocarbons	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a food preservative as a fungicide and fumigant	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during hydroxypropylating of wheat flour in order to modify it to mix readily with water	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If propylene oxide gets into the eyes, wash eyes immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If propylene oxide gets on the skin, immediately wash the contaminated skin with water if propylene oxide has not already evaporated. If propylene oxide soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of propylene oxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If propylene oxide has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If propylene oxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities may be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Propylene oxide should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Propylene oxide may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Propylene Oxide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List,* 1974 Edition, HEW Publication No. 74-134, 1974.
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- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Patty, F. A. (ed.): *Toxicology,* Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Propylene Oxide,* New York, 1971.

* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man,* Volume 11, 1976.

RESPIRATORY PROTECTION FOR PROPYLENE OXIDE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister.
2000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of propylene oxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for n-Propyl Nitrate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_3H_7NO_3$
- Synonyms: None
- Appearance and odor: Colorless to pale yellow liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for n-propyl nitrate is 25 parts of n-propyl nitrate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 110 milligrams of n-propyl nitrate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Propyl nitrate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Animal studies show that n-propyl nitrate causes temporary low blood pressure and may affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause bluish discoloration of the skin, headache, weakness, drowsiness, nausea, rapid heart beat, shortness of breath, and unconsciousness.

2. Long-term Exposure: In animals repeated or prolonged exposure to n-propyl nitrate has caused irritation and thickness of the skin. It may also cause anemia.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to n-propyl nitrate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to n-propyl nitrate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, cardiovascular system, skin, nervous system, and kidneys should be stressed.

—A complete blood count: n-Propyl nitrate has been shown to cause methemoglobinemia in animals. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

n-Propyl nitrate vapor causes anoxia due to the formation of methemoglobin. Exposure of rats to 10,000 ppm for 4 hours caused nasal irritation, dyspnea, methemoglobinemia, weakness, cyanosis, and death. In dogs repeatedly exposed to 260 ppm for 26 weeks, hemoglobinuria and mild anemia appeared during the first 2 weeks of exposure but then subsided. n-Propyl nitrate may induce hypotension in animals by direct action on vascular muscles. The liquid when placed into the eyes of rabbits caused mild transient inflammation with no evidence of corneal damage. The liquid applied to the skin of rabbits daily for 10 days caused staining, inflam-

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mation, and thickening of the skin but no evidence of systemic toxicity. n-Propyl nitrate has the potential to form methemoglobin in man; the effects of methemoglobinemia result from anoxia and include cyanosis especially evident in the lips, nose, and ear lobes; other effects are weakness, dizziness, and severe headache.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 105.1
2. Boiling point (760 mm Hg): 111 C (231 F)
3. Specific gravity (water = 1): 1.06
4. Vapor density (air = 1 at boiling point of n-propyl nitrate): 3.6
5. Melting point: Less than −101 C (−150 F)
6. Vapor pressure at 20 C (68 F): 18 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with either strong oxidizers or with combustibles may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving n-propyl nitrate.
4. Special precautions: n-Propyl nitrate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 20 C (68 F) (closed cup)
2. Autoignition temperature: 175 C (347 F)
3. Flammable limits in air, % by volume: Lower: 2; Upper: 100
4. Extinguishant: Foam, dry chemical

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, "the odor is stated to be detectable at 50 ppm and above."
2. Eye Irritation Level: n-Propyl nitrate is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since its odor threshold is only twice the permissible exposure limit, n-propyl nitrate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure n-propyl nitrate may be used. An analytical method for n-propyl nitrate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid n-propyl nitrate.
- Clothing wet with n-propyl nitrate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of n-propyl nitrate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the n-propyl nitrate, the person performing the operation should be informed of n-propyl nitrate's hazardous properties.
- Non-impervious clothing which becomes contaminated with n-propyl nitrate should be removed promptly and any clothing which becomes wet with liquid n-propyl nitrate should be removed immediately and not reworn until the n-propyl nitrate is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid n-propyl nitrate may contact the eyes.

SANITATION

- Skin that becomes contaminated with n-propyl nitrate should be promptly washed or showered with soap or mild detergent and water to remove any n-propyl nitrate.
- Employees who handle liquid n-propyl nitrate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to n-propyl nitrate may occur and control methods which may be effective in each case:

Operation	Controls
Use in liquid rocket propellants	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid n-propyl nitrate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid n-propyl nitrate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid n-propyl nitrate soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of n-propyl nitrate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid n-propyl nitrate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If n-propyl nitrate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, stir with a solution of sodium hydroxide or soda ash in water until oily layer disappears, then flush. Large quantities can be burned under the supervision of personnel qualified to dispose of explosives. Liquid n-propyl nitrate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of n-propyl nitrate vapors are permitted.

- Waste disposal method:

n-Propyl nitrate may be disposed of as described above.

REFERENCES

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RESPIRATORY PROTECTION FOR N-PROPYL NITRATE

Condition	**Minimum Respiratory Protection* Required Above 25 ppm**
Vapor Concentration	
250 ppm or less	Any chemical cartridge respirator with a cartridge containing non-combustible sorbents and providing protection against n-propyl nitrate. Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and a cartridge containing non-combustible sorbents and providing protection against n-propyl nitrate. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against n-propyl nitrate. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-combustible sorbents and providing protection against n-propyl nitrate. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Pyrethrum

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: The synonyms and molecular weights listed below correspond to the various components of pyrethrum whose formulas are listed here: 1) $C_{21}H_{28}O_3$; 2) $C_{22}H_{28}O_5$; 3) $C_{20}H_{28}O_3$; 4) $C_{21}H_{28}O_5$; 5) $C_{21}H_{30}O_3$; 6) $C_{22}H_{30}O_5$
- Synonyms: 1) Pyrethrin I; 2) Pyrethrin II; 3) Cinerin I; 4) Cinerin II; 5) Jasmolin I; 6) Jasmolin II
- Appearance and odor: Viscous brown resin or solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pyrethrum is 5 milligrams of pyrethrum per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pyrethrum can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

The chief effect from exposure to pyrethrum is skin rash particularly on moist areas of the skin. The rash may be associated with intense itching and blister formation. Hay fever-like symptoms, wheezing, and breathing difficulties may occur from exposure to this chemical. An allergic reaction causing weakness and collapse may occur in sensitive individuals. Pyrethrum may irritate the eyes. In animals, effects of intoxication include convulsions and paralysis.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to pyrethrum.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pyrethrum at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from pyrethrum exposure.

—Chronic respiratory disease: In persons with chronic respiratory disease and especially asthma, the inhalation of pyrethrum might cause exacerbation of symptoms due to its sensitizing properties.

—Skin disease: Pyrethrum can cause dermatitis which may be allergic in nature. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Pyrethrum dust causes dermatitis and occasionally sensitization. In animals, effects of intoxication are excitation, convulsions, muscular fasciculations, and tetanic paralysis. The chief effect in humans from exposure to pyrethrum is dermatitis. The usual lesion is a mild erythematous dermatitis with vesicles, papules in moist areas, and intense pruritis; a bullous dermatitis may develop. In a study of workers engaged in processing pyrethrum powder, 30% had erythema, skin roughening, and pruritis which subsided upon cessation of exposure. One of these workers had an anaphylactic type reaction; shortly after entering a dust laden room, the facial skin turned red and the person felt a sensation of burning and itching; the cheeks and eyes rapidly became swollen and pruritis became severe; the entire condition disappeared in 2 days after removal from

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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exposure. Some persons exhibit sensitivity similar to pollinosis with sneezing, nasal discharge, and nasal stuffiness. A few cases of asthma due to pyrethrum mixtures have been reported; some of the individuals involved had a previous history of asthma with allergy to a wide spectrum of substances.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 1) 328.4; 2) 372.4; 3) 316.4; 4) 360.4; 5) 330.4; 6) 374.4;
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 1 (approximately)
4. Vapor density (air = 1 at boiling point of pyrethrum): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None.
4. Special precautions: None.

- **Flammability**

1. Flash point: 82 – 88 C (180 – 190 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Carbon dioxide, foam, dry chemical

- **Warning properties**

Since the vapor pressure of pyrethrum is essentially zero, warning properties are not considered.

Grant states that pyrethrum "is an insecticide powder which may cause allergic reaction and contact dermatitis. Transient conjunctival edema and hyperemia may be induced. The constituents pyrethrin I and II in pure form are said to be irritating to the eyes and mucous membranes. No persistent ocular disturbance from pyrethrum or its derivatives appears to have been reported."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for pyrethrum is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with pyrethrum or liquids containing pyrethrum where skin contact may occur.
- If employees' clothing may have become contaminated with pyrethrum or liquids containing pyrethrum, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with pyrethrum should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pyrethrum from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pyrethrum, the person performing the operation should be informed of pyrethrum's hazardous properties.
- Non-impervious clothing which becomes contaminated with pyrethrum should be removed promptly and not reworn until the pyrethrum is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where pyrethrum or liquids containing pyrethrum may contact the eyes.

SANITATION

- Skin that becomes contaminated with pyrethrum should be promptly washed or showered with soap or mild detergent and water to remove any pyrethrum.
- Employees who handle pyrethrum or liquids containing pyrethrum should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pyrethrum may occur and control methods which may be effective in each case:

Operation	Controls
Application as an insecticide on pre- and post-harvest agricultural crops; cattle and poultry, food cartons, and confined areas	Good personal hygiene
Manufacture of pyrethrum	Good personal hygiene
Formulation of scabicides and parasiticides for medical and veterinary use	Good personal hygiene

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If pyrethrum or liquids containing pyrethrum get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If pyrethrum or liquids containing pyrethrum get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If pyrethrum or liquids containing pyrethrum penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of pyrethrum, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When pyrethrum or liquids containing pyrethrum have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If pyrethrum is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.

- Waste disposal methods:

Pyrethrum may be disposed of:

1. By making packages of pyrethrum in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving pyrethrum in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PYRETHRUM

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of pyrethrum; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 5000 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Pyridine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_5H_5N
- Synonyms: None
- Appearance and odor: Colorless or yellow liquid with a penetrating, sickening odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pyridine is 5 parts of pyridine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 15 milligrams of pyridine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pyridine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to pyridine may cause irritation of the eyes, skin, and lining of the respiratory tract. Heavy exposure may also cause gastrointestinal disturbances with diarrhea, abdominal pain, and nausea, weakness, headache, dizziness, difficulty in sleeping, nervousness, and back pain with urinary frequency. Damage to the liver and kidneys may occur. There is some evidence that permanent central nervous system damage may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to pyridine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pyridine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Kidney damage has been reported from oral administration of pyridine to humans for therapeutic purposes. A urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Pyridine may cause liver damage. A profile of liver function should be performed by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Pyridine vapor is a mild irritant to eyes and mucous membranes, and at high concentrations causes narcosis. In animals the major effects from administration of large doses by any route are local irritation and narcosis, while repeated feeding results in kidney and liver injury. Fatal injury to the liver and kidney has been reported from the prolonged oral administration of 1.8 to 2.5 ml daily for human therapeutic purposes. Workers exposed repeatedly to vapor concentrations averaging 125 ppm developed nausea and anorexia, as well as headache, dizziness, nervousness, and insomnia; in some cases, lower abdominal or back discomfort with urinary frequency was observed without associated evidence of liver or kidney damage. The possibility of permanent central nervous system injury is suggested by some case

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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reports. Chemical plant workers exposed to pyridine at a concentration of 6 to 12 ppm developed headache, temporary vertigo, nervousness, sleeplessness, nausea, and vomiting. In the eye of a rabbit a 40% solution caused corneal necrosis. Skin irritation may result from prolonged or repeated contact with the vapor and liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 79
2. Boiling point (760 mm Hg): 115.3 C (239 F)
3. Specific gravity (water = 1): 0.98
4. Vapor density (air = 1 at boiling point of pyridine): 2.72
5. Melting point: −42 C (−43.6 F)
6. Vapor pressure at 20 C (68 F): 18 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause violent spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving pyridine.
4. Special precautions: Liquid pyridine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 20 C (68 F) (closed cup)
2. Autoignition temperature: 482 C (900 F)
3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 12.4
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Stern reports an odor threshold of 0.23 ppm, Summer reports 0.012 ppm, and May reports 0.013 ppm. The AIHA *Hygienic Guide*, however, notes that the odor "is an unreliable guide to concentrations exceeding 5 ppm. Olfactory fatigue occurs quickly."
2. Eye Irritation Level: Grant reports that the vapor of pyridine is irritating to the eyes, but he gives no quantitative information.
3. Other Information: Grant reports that pyridine vapors cause respiratory tract irritation, but no quantitative information is given. Persons who handle pyridine report that although olfactory fatigue occurs rapidly, a definite taste remains, thus giving adequate warning of exposure.
4. Evaluation of Warning Properties: Although olfactory fatigue occurs rapidly upon exposure to pyridine, a definite taste remains. For this reason, pyridine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of pyridine vapors using an adsorption tube with subsequent desorption with methylene chloride and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure pyridine may be used. An analytical method for pyridine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid pyridine or solutions containing pyridine, where skin contact may occur.
- Clothing contaminated with pyridine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

pyridine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pyridine, the person performing the operation should be informed of pyridine's hazardous properties.

- Where exposure of an employee's body to liquid pyridine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with pyridine should be removed promptly and not reworn until the pyridine is removed from the clothing.
- Any clothing which becomes wet with liquid pyridine should be removed immediately and not reworn until the pyridine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid pyridine or solutions containing pyridine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid pyridine or solutions containing pyridine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with pyridine should be immediately washed or showered to remove any pyridine.
- Employees who handle liquid pyridine or solutions containing pyridine should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pyridine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of pharmaceuticals such as antihistamines, vitamins, medicinals, CNS stimulants, and local anesthetics	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent in manufacture of polycarbonate resins used in hand tools, small appliances, camera parts, safety helmets, and electrical connectors	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a starting material in manufacture of chemical intermediates and products; use in manufacture of rubber accelerators, epoxy resins, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent reaction medium or catalyst in paint manufacture, carbohydrate treatment, drug manufacture, and rubber manufacture; use as a reagent in chemical analysis	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in textile treatment as a water-proofing agent; use as a denaturant for ethyl alcohol; use as a coupling assistant in azo dye manufacture; use in purification of mercury fulminate in explosives manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
During thermal decomposition of flexible polyurethane foams	Personal protective equipment
Use as an inhibitor and for preparation of inhibitors; use in oil and gas well drilling	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid pyridine or solutions containing pyridine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid pyridine or solutions containing pyridine get on the skin, immediately flush the contaminated skin with water. If liquid pyridine or solutions containing pyridine penetrate through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of pyridine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When pyridine has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If pyridine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Pyridine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Pyridine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR PYRIDINE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
250 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3600 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3600 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of pyridine; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 3600 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Quinone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: OC_6H_4O
- Synonyms: p-Benzoquinone
- Appearance and odor: Pale yellow solid with an acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for quinone is 0.1 part of quinone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of quinone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Quinone can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

If quinone comes in contact with the skin or the lining of the nose and throat, it may cause irritation, discoloration, redness, swelling, and blistering. Prolonged contact with the skin may cause ulceration. Contact with the eyes may cause irritation, discoloration, and damage which may produce vision difficulties and may be permanent.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to quinone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to quinone at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of congenital or acquired eye defects would be expected to be at increased risk from exposure. Persons with poor visual acuity from high degrees of astigmatism, keratoconus, or pre-existing corneal injury should be excluded from repeated, uncontrolled exposure to quinone vapor. Examination of the eyes and skin should be stressed.

—Opthalmic examination: Quinone causes eye damage in humans. An opthalmic examination should be performed, including visual acuity and slit-lamp inspection of the cornea.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Quinone is a solid with appreciable vapor pressure, and the vapor or dust is very hazardous to the eyes. Acute exposure causes conjunctival irritation, and in some cases corneal edema, ulceration and scarring; transient eye irritation may be noted above 0.1 ppm and becomes marked at 1 to 2 ppm. Chronic exposure causes the gradual development of changes characterized as: (1) brownish discoloration of the conjunctiva and cornea confined to the intrapalpebral fissure, (2) small opacities of the cornea, and (3) structural corneal changes which result in loss of visual acuity. The pigmentary changes are reversible, but the more slowly developing structural changes in the cornea may progress. Although pigmentation may occur with less than 5 years of exposure, serious injury. Skin contact may cause irritation and

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this is uncommon and usually is not associated with serious injury. Skin contact may cause irritation and staining. Systemic effects from industrial exposure have not been reported. Skin cancer has been reported in mice painted with a quinone solution. A 0.1% or 0.25% solution of quinone in benzene was applied to the skin of mice daily or every other day; of 87 mice surviving for 200 days, 9 had papillomas of the skin, 3 had cancer of the skin, and 8 had lung cancer.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 108.1
2. Boiling point (760 mm Hg): Sublimes
3. Specific gravity (water = 1): 1.32
4. Vapor density (air = 1 at boiling point of quinone): 3.7
5. Melting point: 113 C (235 F)
6. Vapor pressure at 20 C (68 F): 0.1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as quinone fumes and carbon monoxide) may be released in a fire involving quinone.
4. Special precautions: Quinone will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Water spray, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, the "odor of quinone is not readily apparent at 0.1 ppm." Grant, however, reports that the "vapors are perceptible by smell to human beings at about 0.1 ppm in air." According to the *Hygienic Guide*, olfactory fatigue occurs upon exposure to quinone.
2. Eye Irritation Level: The *Hygienic Guide* states that "transient eye irritation may be noted above 0.1 ppm and becomes marked at 1 to 2 ppm." Grant states that "at 0.5 ppm the vapors are irritating to the eyes and at 3.0 ppm they are very irritating."
3. Evaluation of Warning Properties: The *Hygienic Guide* states that "exposure evaluation by odor and irritant effects is not adequate to assure safety because: 1) the odor of quinone is not readily apparent at 0.1 ppm, 2) olfactory fatigue occurs, and 3) repeated exposure to levels causing sensory irritation may cause chronic eye injury." For these reasons, quinone is treated as a material with poor warning properties. The concentration of quinone in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for quinone is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with quinone, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with quinone, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing which has had any possibility of being contaminated with quinone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of quinone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the quinone, the person performing the operation should be informed of quinone's hazardous properties.
- Where exposure of an employee's body to solid quinone or liquids containing quinone may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with quinone should be removed immediately and not reworn until the quinone is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of quinone or liquids containing quinone contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid quinone or liquids containing quinone, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with quinone should be immediately washed or showered with soap or mild detergent and water to remove any quinone.
- Workers subject to skin contact with quinone should wash with soap or mild detergent and water any areas of the body which may have contacted quinone at the end of each work day.
- Eating and smoking should not be permitted in areas where quinone is handled, processed, or stored.
- Employees who handle quinone should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to quinone may occur and control methods which may be effective in each case:

Operation	Controls
Use as an oxidizing agent in synthesis of organic chemicals and intermediates; in photography—developer hydroquinone; in agriculture in production of insecticides and fungicides; in pharmaceutical industry for production of cortisone and addition compound with barbituates	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer and resins industry as an inhibitor and retarder-antioxidant, curing agent, and catalyst	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a toner and intensifier in photographic industry; as a tanning agent for leather industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of quinhydrone electrodes for use for pH determinations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid quinone or liquids containing quinone get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If quinone gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If quinone penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of quinone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When quinone has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If quinone is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Quinone may be disposed of:

1. By making packages of quinone in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving quinone in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR QUINONE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Particulate or Vapor Concentration	
5 ppm or 20 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
75 ppm or 300 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 75 ppm or 300 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Rhodium Metal Fume and Dusts (as Rhodium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Rh
- Synonyms: None
- Appearance: Gray fume or dust.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for rhodium metal fume and dusts is 0.1 milligram of rhodium metal fume and dusts (as rhodium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

None: See "Summary of toxicology."

- **Effects of overexposure**

1. Short-term Exposure: None known.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to rhodium metal fume and dusts.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to rhodium metal fume and dusts at potentially hazardous levels.

- **Summary of toxicology**

No toxic effects of rhodium metal fume and dusts have been reported from animal experiments or from observations on human beings.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.9
2. Boiling point (760 mm Hg): Above 2500 C (4532 F)
3. Specific gravity (water = 1): 12.4
4. Vapor density (air = 1 at boiling point of rhodium metal fume and dusts): Not applicable
5. Melting point: 1966 C (3570 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Rhodium metal fume and dusts are not known to be eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of rhodium metal fume and dusts on a filter, followed by

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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treatment with nitric acid, solution in hydrochloric acid, treatment with potassium bisulfate, and atomic absorption spectrophotometric analysis. An analytical method for rhodium metal fume and dusts is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to rhodium metal fume and dusts may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of platinum alloys for use in thermocouples, windings for resistance furnaces, laboratory crucibles and catalysts for chemical processing, and preparation of dental castings	General dilution ventilation; local exhaust ventilation
Liberation during production and casting of rhodium powder during refining and recovery	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in applying thin reflective coatings by sublimation to scientific instruments, radio and radar equipment, searchlight reflectors, cinema projections, and headlight reflectors	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of rhodium metal fume and dusts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When rhodium metal dust has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention.

SPILL AND DISPOSAL PROCEDURES

- If potentially hazardous amounts of rhodium metal fume and dusts are spilled or inadvertently released, the following steps should be taken:

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Rhodium metal dusts may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Rhodium as Rh," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR RHODIUM METAL FUME AND DUSTS (AS RHODIUM)

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m³**
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator.
1 mg/m³ or less	Any fume respirator or high efficiency particulate respirator. Any dust and mist respirator, except single-use or quarter-mask respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Rhodium Salts (as Rhodium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble rhodium salts. Physical and chemical properties of one specific compound are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION—Hydrated rhodium trichloride

- Formula: $RhCl_3$-xH_2O
- Synonyms: Soluble rhodium trichloride; rhodium chloride
- Appearance and odor: Red-brown, odorless solid or liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble rhodium salts is 0.001 milligram of soluble rhodium salts (as rhodium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble rhodium salts may affect the body if they are inhaled or if they come in contact with the eyes or skin. They may also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: None known in humans

2. Long-term Exposure: None known in humans

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble rhodium salts.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble rhodium salts at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble rhodium salts exposure.

—Eye disease: Rhodium chloride has caused eye damage in animals. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although rhodium is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Central nervous system disorders: Rhodium trichloride has caused central nervous system damage in animals. Individuals with pre-existing central nervous system disorders may be more susceptible.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Toxicologic data on the soluble salts of rhodium are meager; however, solutions of salts splashed in the eye may cause mild irritation. Rhodium trichloride was found to have chemotherapeutic action against certain viruses in mice, but no mention was made of toxicity. The LD50 for rhodium trichloride in rabbits by intravenous injection was 215 mg/kg; the clinical signs presented shortly after injection were increasing lethargy and waning respiration. There were no abnormal findings at autopsy, and the rapid onset of death suggested central nervous system effects. A solution of rhodium chloride in a rabbit eye gave a delayed injurious reaction; a 0.1-M solution adjusted to pH 7.2 with ammonium hydroxide was placed for 10 minutes in a rabbit eye after the corneal epithelium had been removed; an orange color-

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ation of the cornea occurred, which faded to faint yellow within 8 weeks. During the first 2 to 3 weeks, the cornea was slightly hazy; in the third week white opacities gradually developed, and finally there was extensive opacification and vascularization. Systemic effects have not been reported from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Hydrated rhodium trichloride**

1. Molecular weight: Greater than 209
2. Boiling point (760 mm Hg): 800 C (1472 F) (sublimes)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of soluble rhodium salts): Not applicable
5. Melting point: 100 C (212 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: At temperatures above 100 C(212 F), some decomposition may occur.
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride or chlorine) may be released when rhodium trichloride decomposes.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

The only rhodium salt for which information is available concerning toxic effects on the eye is rhodium chloride. Grant states that "rhodium chloride has been tested on a rabbit's eye and was found to give a peculiar delayed injurious reaction. A O.1-M clear, dark-red solution prepared and adjusted to pH 7.2 with ammonium hydroxide was applied for 10 minutes to the eye after the corneal epithelium had been removed by scraping. This exposure caused orange coloration of the cornea, fading to faint yellow in the course of 2 months. During the first 2 to 3 weeks the cornea was not opaque, but was slightly hazy. In the third week, however, irregular white opacities gradually developed. Ultimately the cornea became extensively opacified and vascularized."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of soluble rhodium salts on a filter, followed by treatment with nitric acid and perchloric acid, solution in aicd, and atomic absorption spectrophotometric analysis. An analytical method for soluble rhodium salts is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4). Analytical Methods for Set M" (order number PB 265 029).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with soluble rhodium salts or liquids containing soluble rhodium salts.
- Clothing contaminated with soluble rhodium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of soluble rhodium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the soluble rhodium salts, the person performing the operation should be informed of soluble rhodium salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with soluble rhodium salts should be removed promptly and not reworn until the soluble rhodium salts are removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble rhodium salts or liquids containing soluble rhodium salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with soluble rhodium salts should be promptly washed or showered to remove any soluble rhodium salts.
- Eating and smoking should not be permitted in areas where soluble rhodium salts or liquids containing soluble rhodium salts are handled, processed, or stored.
- Employees who handle soluble rhodium salts or liquids containing soluble rhodium salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble rhodium salts may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during refining and extraction of metal from platinum ores	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in electroplating baths for finishing scientific instruments, camera fittings, radio equipment, and jewelry; use in laboratory for research	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If soluble rhodium salts or liquids containing soluble rhodium salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.

- **Skin Exposure**

If soluble rhodium salts or liquids containing soluble rhodium salts get on the skin, flush the contaminated skin with water. If soluble rhodium salts or liquids containing soluble rhodium salts penetrate through the clothing, remove the clothing and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble rhodium salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble rhodium salts or liquids containing soluble rhodium salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble rhodium salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble rhodium salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble rhodium salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR SOLUBLE RHODIUM SALTS (AS RHODIUM)

Condition	**Minimum Respiratory Protection* Required Above 0.001 mg/m³**
Particulate Concentration	
0.01 mg/m³ or less	Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
0.05 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Ronnel

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula:$(CH_3O)_2PSOC_6H_2Cl_3$
- Synonyms: Fenchlorphos; O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate
- Appearance and odor: White to tan waxy solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ronnel is 15 milligrams of ronnel per cubic meter of air (mg/m^3) averaged over an eight-hour work shift (*Federal Register*, Vol. 43, p. 57603, 8 December 1978).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ronnel can affect the body if it is inhaled or if it comes in contact with the eyes. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Ronnel is one of the least toxic of the organophosphate insecticides. Very large exposures are required to cause symptoms. In animal experiments, ronnel has caused watering of the mouth, tremors, diarrhea, small pupils, and respiratory distress. Ronnel powder is irritating to the eye in rabbits.

2. Long-term Exposure: In animals ronnel has caused liver and kidney damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ronnel.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ronnel at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ronnel exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ronnel might cause exacerbation of symptoms due to an anticholinesterase effect.

—Liver disease: Ronnel causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Ronnel causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ronnel is a weak cholinesterase inhibitor. It affects primarily the pseudoesterases of the blood plasma rather than the erythrocyte acetylcholinesterase. In male rats, the oral LD50 was 1.7 g/kg; effects were salivation, tremors, diarrhea, miosis, and respiratory distress – all attributed to the anticholinesterase effect of ronnel. Rats fed 50 mg/kg body weight in the diet for 105 days developed slight liver and kidney damage. When a small amount of ronnel powder was placed in the eye of a rabbit, there were slight discomfort and transient conjunctival irritation which subsided within 48 hours. In an experiment on humans in which 50 subjects received 3 applications per week for 3 weeks of

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gauze saturated with a 10% suspension of ronnel in sesame oil, there were no significant effects on the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 321.5
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.48
4. Vapor density (air = 1 at boiling point of ronnel): Not applicable
5. Melting point: 35 C (95 F)
6. Vapor pressure at 20 C (68 F): 0.0008 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0044
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 150 C (300 F) may cause explosive decomposition and formation of toxic gases.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, dimethyl sulfide, trichlorophenol, etc., and carbon monoxide) may be released when ronnel decomposes.
4. Special precautions: Melted ronnel will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Ronnel may cause mild eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for ronnel is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with ronnel or liquids containing ronnel.
- If employees' clothing may have become contaminated with ronnel or liquids containing ronnel, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with ronnel should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ronnel from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ronnel, the person performing the operation should be informed of ronnel's hazardous properties.
- Non-impervious clothing which becomes contaminated with ronnel should be removed promptly and not reworn until the ronnel is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where ronnel or liquids containing ronnel may contact the eyes.

SANITATION

- Skin that becomes contaminated with ronnel should be promptly washed or showered with soap or mild detergent and water to remove any ronnel.
- Eating and smoking should not be permitted in areas where solid ronnel is handled, processed, or stored.
- Employees who handle ronnel or liquids containing ronnel should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ronnel may occur and control methods which may be effective in each case:

Operation	Controls
Use as an insecticide and pest control agent for agricultural and livestock operations	General dilution ventilation; personal protective equipment
Formulation of insecticides for agricultural and livestock use	General dilution ventilation; personal protective equipment
Use as an insecticide for fruits	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If ronnel or liquids containing ronnel get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If ronnel or liquids containing ronnel get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If ronnel or liquids containing ronnel penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ronnel, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ronnel or liquids containing ronnel have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If ronnel is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Molten ronnel should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Ronnel may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR RONNEL

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
150 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust, fume, and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7500 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Rotenone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{23}H_{22}O_6$
- Synonyms: Rotenone, commercial; tubatoxin; "cube"; derrin
- Appearance and odor: Colorless to red, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for rotenone is 5 milligrams of rotenone per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Rotenone can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to rotenone may cause irritation of the eyes and skin. Symptoms of absorption of rotenone dust (inferred mostly from animal studies) include numbness of the mouth, nausea, vomiting, gastric pain, pulmonary irritation, trembling, loss of coordination, convulsions, stupor, and cessation of breathing. In animal experiments, exposure to rotenone dust has caused liver and kidney damage and has produced tumors.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to rotenone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to rotenone at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, eyes, respiratory tract, and liver should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Rotenone dust affects the nervous system and causes convulsions in animals. Animals repeatedly fed derris powder (a botanical source containing 9.6% rotenone) at levels from 312 to 5000 ppm developed focal liver necrosis and mild kidney damage. Of 40 female rats given daily intraperitoneal injections of rotenone in sunflower oil of 1.7 mg/kg for 42 days, over 60% developed mammary tumors 6 to 11 months after the end of treatment; most of the tumors were mammary adenomas; one was a differentiated adenocarcinoma; none of the control animals had tumors when examined 19 months after treatment. The lethal oral dose in humans is estimated to be 0.3 to 0.5 g/kg. In humans, inhalation of dust is expected to cause pulmonary irritation. Symptoms of absorption in humans (inferred mostly from animal studies) may include numbness of oral mucous membranes, nausea, vomiting, and abdominal pain. There may be muscle tremors, incoordination, clonic convulsions, and stupor. The dust is irritating to the eyes and skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 394.4
  2. Boiling point (760 mm Hg): Decomposes

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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3. Specific gravity (water = 1): 1 (approximately)

4. Vapor density (air = 1 at boiling point of rotenone): Not applicable

5. Melting point: 163 C (325 F) or 181 C (358 F)

6. Vapor pressure at 20 C (68 F): Essentially zero

7. Solubility in water, g/100 g water at 20 C (68 F): 0.00002

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: None.

4. Special precautions: None.

- **Flammability**

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Foam, carbon dioxide, dry chemical, water.

- **Warning properties**

Since the vapor pressure of rotenone is negligible, warning properties are not considered.

Rotenone is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for rotenone is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with rotenone or liquids containing rotenone.
- If employees' clothing has had any possibility of being contaminated with rotenone or liquids containing rotenone, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with rotenone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of rotenone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the rotenone, the person performing the operation should be informed of rotenone's hazardous properties.
- Non-impervious clothing which becomes contaminated with rotenone should be removed promptly and not reworn until the rotenone is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where rotenone or liquids containing rotenone may contact the eyes.

SANITATION

- Skin that becomes contaminated with rotenone should be promptly washed or showered with soap or mild detergent and water to remove any rotenone.
- Eating and smoking should not be permitted in areas where rotenone or liquids containing rotenone is handled, processed, or stored.
- Employees who handle rotenone or liquids containing rotenone should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to rotenone may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticides	Process enclosure; local exhaust ventilation; wet methods
Application on agricultural crops and livestock as an insecticide and ascaricide	Personal protective equipment
Manufacture of rotenone	Process enclosure; local exhaust ventilation; wet methods; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If rotenone or liquids containing rotenone get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If rotenone or liquids containing rotenone get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If rotenone or liquids containing rotenone penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of rotenone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When rotenone or liquids containing rotenone have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If rotenone is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities can be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.

- Waste disposal methods:

Rotenone may be disposed of

1. By making packages of rotenone in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving rotenone in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ROTENONE (COMMERCIAL)

Condition	**Minimum Respiratory Protection* Required Above 5 mg/m^3**
Particulate Concentration	
50 mg/m^3 or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m^3 or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m^3 or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Selenium and Its Inorganic Compounds (as Selenium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all selenium and its inorganic compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Selenium

- Formula: Se
- Synonyms: Selenium, metallic; selenium, elemental
- Appearance and odor: Black, gray, or red odorless solid.

Sodium selenite

- Formula: Na_2SeO_3
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Sodium selenate

- Formula: Na_2SeO_4
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium dioxide

- Formula: SeO_2
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium oxychloride

- Formula: $SeOCl_2$
- Synonyms: None
- Appearance: Colorless to yellow liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium and its inorganic compounds is 0.2 milligram of selenium and its inorganic compounds (as selenium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect the body if they are inhaled, if they come in contact with the eyes or skin, or if they are swallowed. Selenium oxychloride and selenium dioxide may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye," an allergy of the eyelids in which they may become puffy.

2. Long-term Exposure: Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen, and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to selenium and its inorganic compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium and its inorganic compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

—Urinalysis: Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Selenium causes liver damage and tumors in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes irritate the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/m^3 for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen, and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage, and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised, based upon observations in animals, but it has not been established in man. Eleven of 53 rats developed adenoma or low-grade carcinoma in cirrhotic livers, and four others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7, or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In control rats 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1%. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea, followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/m^3, while urinary levels ranged from below 0.10 to 0.43 mg/l; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred, and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide, which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Selenium**
  1. Molecular weight: 78.96
  2. Boiling point (760 mm Hg): 685 C (1265 F)
  3. Specific gravity (water = 1): 4.45 to 4.8
  4. Vapor density (air = 1 at boiling point of selenium): Not applicable
  5. Melting point: 150 C (302 F)
  6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Sodium selenite**
  1. Molecular weight: 173
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 3.1
  4. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
  5. Melting point: 710 C (1310 F) (decomposes)
  6. Vapor pressure at 20 C (68 F): Less than 0.001 mg Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 85
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Sodium selenate**
  1. Molecular weight: 188.9
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 3.1

4. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable

5. Melting point: Decomposes

6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg

7. Solubility in water, g/200 g water at 20 C (68 F): 83

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Selenium dioxide**

1. Molecular weight: 110.9

2. Boiling point (760 mm Hg): 315 C (599 F) (sublimes)

3. Specific gravity (water = 1): 3.95

4. Vapor density (air = 1 at boiling point of selenium dioxide): Not applicable

5. Melting point: 340 C (644 F)

6. Vapor pressure at 20 C (68 F): 0.001 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 257

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Selenium oxychloride**

1. Molecular weight: 165.9

2. Boiling point (760 mm Hg): 176 C (349 F)

3. Specific gravity (water = 1): 2.42

4. Vapor density (air = 1 at boiling point of selenium oxychloride): 5.7

5. Melting point: 10.8 C (51 F)

6. Vapor pressure at 20 C (68 F): 0.35 mm approximately

7. Solubility in water, g/100 g water at 20 C (68 F): Decomposes

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous

2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride.

4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable

2. Autoignition temperature: Selenium: Data not available; sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride: Not applicable

3. Flammable limits in air, % by volume: Not applicable

4. Extinguishant: For selenium, water

- **Warning properties**

The *Documentation of TLV's* notes that "Clinton reported intense irritation of eyes, nose, and throat, followed by headache, in a group of workers briefly exposed to high concentrations of selenium fume." The ILO reports that "persons who work in atmospheres containing selenium dioxide dust may develop a condition known among the workers as 'rose eye,' a pink allergy of the eyelids, which often become puffy. There is usually also a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctiva." The *Hygienic Information Guide* for selenium states that "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." Grant reports that both selenium dioxide and selenium sulfide can produce toxic effects on the eye. Quantitative information concerning air concentrations of selenium compounds which cause eye irritation is not available.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of selenium and its inorganic compounds on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for selenium and its inorganic compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with selenium oxychloride or liquids containing selenium oxychloride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with selenium dioxide or liquids containing selenium dioxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite,sodium selenate, selenium dioxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to selenium, selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with selenium oxychloride should be removed immediately and not reworn until the selenium oxychloride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of selenium dioxide, selenium oxychloride, or liquids containing these compounds contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to selenium oxychloride, selenium dioxide, or liquids containing these compounds, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds at the end of each work day.
- Skin that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these substances should be promptly washed or showered to remove any contaminant.
- Skin that becomes contaminated with selenium oxychloride should be immediately washed or showered to remove any selenium oxychloride.
- Eating and smoking should not be permitted in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to selenium and its inorganic compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining recovery, and purification and manufacture of selenium compounds	Local exhaust ventilation; general . dilution ventilation; personal protective equipment

Operation	Controls
Use in glassware industry for decolorization of fiberglass, scientific glassware, vehicular tail lights, traffic and other signal lenses, and infrared equipment; use in manufacture of electrical components in welding, transformers, semiconductors, photoelectric cells, etc.	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photography and photocopy devices; manufacture of dyes, pigments, and colored glazes for metal etching and for printing on glass	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of lubricating oils and extreme pressure lubricants as antioxidants and detergency improvers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry for manufacture and use as vulcanization accelerators and antioxidants; use in manufacture of pharmaceuticals, fungicides, and dermatitis control	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst for hardening fats for soaps, waxes, edible fats, and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, parasiticides, bactericides, and herbicides for agricultural and citrus crops	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of flame-proofing agents on textiles and electric cables	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of delayed action blasting caps	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as solvents in paint and varnish removers; rubber, resin, and glue solvent; use for organic synthesis in oxidation, hydrogenation, and dehyrogenation	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in refining of copper, silver, gold, or nickel ores or during recycling of scrap metal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous operations in manufacture of insect repellants, activators, hardeners, special ceramic materials, plasticizers, and mercury vapor detectors	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use for preparation of feed additives for poultry and swine	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If selenium or its inorganic compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If selenium or its inorganic compounds get on the skin, immediately wash the contaminated skin. If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through the clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of selenium sodium selenite, sodium selenate, or selenium dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When selenium, sodium selenite, sodium selenate, selenium oxychloride, or selenium dioxide have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If selenium or its inorganic compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing selenium and its inorganic compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Selenium and its inorganic compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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* SPECIAL NOTE

Selenium and its inorganic compounds (as selenium) appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

RESPIRATORY PROTECTION FOR SELENIUM AND ITS INORGANIC COMPOUNDS (AS SELENIUM)

Condition	**Minimum Respiratory Protection* Required Above 0.2 mg/m³**
Particulate Concentration	
10 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
Greater than 100 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Selenium Hexafluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: SeF_6
- Synonyms: None
- Appearance: Colorless gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium hexafluoride is 0.05 part of selenium hexafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of selenium hexafluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Selenium hexafluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Animal experiments have shown selenium hexafluoride to be a severe respiratory irritant which has produced severe breathing difficulties. These breathing difficulties may be delayed in onset.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to selenium hexafluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium hexafluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Selenium hexafluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Selenium hexafluoride is a severe pulmonary irritant in animals. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Pericdic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Selenium hexafluoride gas is a severe respiratory irritant in animals. Exposure of four animal species to 10 ppm for 4 hours was fatal; 5 ppm for 4 hours was not fatal but caused pulmonary edema, while 1 ppm produced no effects. Animals exposed to 5 ppm for 1 hour daily for 5 days developed signs of pulmonary injury; 1 ppm for the same time period caused no detectable effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 193
2. Boiling point (760 mm Hg): −35 C (−31 F)
3. Specific gravity (water = 1): 2.3 (liquid)
4. Vapor density (air = 1 at boiling point of selenium hexafluoride): 6.7
5. Melting point: −39 C (−38 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble; reacts slowly

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8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Data not available
4. Special precautions: None

- **Flammability**

1. Not combustible
2. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of selenium hexafluoride.
2. Eye Irritation Level: There is no indication in the available toxicological information that selenium hexafluoride produces eye irritation. Concerning fluorides, however, Grant states that "irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m^3 of air."
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of selenium hexafluoride, this compound is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure selenium hexfluoride may be used. An analytical method for selenium hexafluoride is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to selenium hexafluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a gaseous electric insulator	Process enclosure; local exhaust ventilation; personal protective equipment
Use during production of selenium hydroxide and hydrofluoric acid, selenium and nitrogen	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of selenium hexafluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If selenium hexafluoride is leaked, the following steps should be taken:

1. Ventilate area of leak.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Selenium Hexafluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Selenium and Compounds," *Hygienic Guide Series,* Detroit, Michigan, 1959.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Patty, F. A. (ed.): *Toxicology,* Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

RESPIRATORY PROTECTION FOR SELENIUM HEXAFLUORIDE

Condition	**Minimum Respiratory Protection* Required Above 0.05 ppm**
Gas Concentration	
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2.5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against selenium hexafluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Amorphous Silica

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: SiO_2
- Synonyms: Diatomite; silicon dioxide (amorphous); diatomaceous earth; diatomaceous silica
- Appearance and odor: Colorless to gray odorless powder.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for amorphous silica is 20 million particles of amorphous silica per cubic foot of air (mppcf) averaged over an eight-hour work shift, or the quotient of 30 mg/m³ divided by the percent of silica present. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for amorphous silica from 20 mppcf to 6 mg/m³ total dust (all sampled dust) and 3 mg/m³ for respirable dust.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Amorphous silica can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

Prolonged inhalation of amorphous silica including uncalcined diatomaceous earth may produce x-ray changes in the lungs without disability. Prolonged inhalation of calcined diatomaceous earth may cause silicosis with scarring of the lungs, cough, and shortness of breath.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to amorphous silica.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to amorphous silica at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Although the contribution of amorphous silica including natural diatomaceous earth to the development of pneumoconiosis is unclear, surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Since persons with impaired pulmonary function may be at increased risk from exposure to amorphous silica, periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Amorphous silica, including natural diatomaceous earth, is usually considered to be of low toxicity; however, pure amorphous silica is rarely found, and diatomaceous earth usually contains some amount of crystalline silica. When converted partially to a crystalline form by calcination, the dust of diatomaceous earth produces pulmonary fibrosis. Repeated exposure of guinea pigs to natural diatomaceous earth for periods up to 50 weeks to average concentrations ranging from 60 to 124 mg/m³ caused thickening of the alveolar septa by infiltration of macrophages, accumulation of large numbers of multinuclear cells containing dust particles, and lymphadenopathy, but no proliferation of connective tissue. In a study of diatomaceous earth workers,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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those employed in the quarry for more than 5 years and exposed only to natural diatomaceous earth had no significant roentgenologic changes; of others employed for more than 5 years in the milling process and exposed to calcined material, 17% had simple pneumoconiosis and 23% had the confluent form, probably the result of fibrogenic action of the crystalline silica formed by calcination of the naturally occurring mineral. In humans, calcined diatomaceous earth pneumoconiosis is characterized roentgenographically by fine linear and/or minute nodular shadows, either or both of which may be accompanied by conglomerate fibrosis; in the simple phase of the disease, the upper lobes, are affected more than the lower lobes and the condition progresses by an increase in the apparent number of the nodules, which rarely attain the density or size of nodules often seen in quartz silicosis. In the early confluent stage of the disease, the linear and nodular changes in the upper lung fields become more circumscribed and homogeneous; histologically, there is an absence of the focal, discrete, hyaline nodules or the whorled pattern of collagenous fibers of typical silicosis. The majority of experimental rats exposed to synthetic submicron amorphous silica at 1.5 mg/ft^3 of air died from pulmonary vascular obstruction coupled with pulmonary insufficiency. Rats that survived recovered almost completely after 6 months.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60.1
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.65
4. Vapor density (air = 1 at boiling point of amorphous silica): Not applicable
5. Melting point: 1700 C (3100 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with fluorine, oxygen dilfuoride, and chlorine trifluoride will cause fire.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Grant states that "particles of silica predominantly in the range of 2u to 3u introduced into the corneal stroma of rabbit eyes cause very little reaction."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of amorphous silica in an impinger, followed by dust counting utilizing an optical microscope. An analytical method for amorphous silica is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to amorphous silica may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during preparation by crushing, screening, calcining, and packing operations for industrial processes	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during mining and quarrying operations in extraction	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use in manufacture of insulating materials including firebrick, insulation blocks, pipe covering, roofing felt, and asbestos panels	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a filter medium in food and beverage manufacture including sugar refining, brewing, wine and spirit manufacture, soft drinks, and purification of oils and fats	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of construction bonding materials including stucco, concrete, cement, plaster, and asphalt; manufacture of abrasive cleaning and polishing agents including scouring and polishing soaps and powders	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings as porous extender and flattening agent in paint; as a filler agent for paints, lacquers, and varnishes; filler in paper manufacture, agricultural chemicals, and mineral filler in manufacture of plastics and vinyls	Process enclosure; local exhaust ventilation; personal protective equipment
Use in dry grinding operations including grinding and polishing with natural abrasive wheels; manufacture of absorbent floor cleaning agents for use in industry, refineries, and gas stations; use as a parting powder in foundry operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of pharmaceuticals and as a constituent of pill masses, dentifrices, and salves; use in pottery manufacture in glazes and bodies; use in water treatment; use as a carrier for nickel catalysts in petroleum and petrochemical industries	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If amorphous silica including diatomaceous earth gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If amorphous silica is spilled or potentially hazardous quantities are released, the following steps should be t

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Amorphous silica may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Silica (Amorphous)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Smart, R. H., and Anderson, W. M.: "Pneumoconiosis Due to Diatomaceous Earth – Clinical and X-Ray Aspects," *Industrial Medicine and Surgery*, 21:509-518, 1952.
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RESPIRATORY PROTECTION FOR AMORPHOUS SILICA (INCLUDING NATURAL AND DIATOMACEOUS EARTH)

Condition	**Minimum Respiratory Protection*** **Required Above 20 mppcf**
Particulate Concentration	
100 mppcf or less	Any dust and mist respirator.
200 mppcf or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
1000 mppcf or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 mppcf or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 10,000 mppcf or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Crystalline Silica

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: SiO_2
- Synonyms: Quartz; coesite; cristobalite; tridymite
- Appearance and odor: Colorless, odorless solid. (Crystalline silica may be a component of many mineral dusts).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for crystalline silica is (for respirable dust) 10 milligrams silica per cubic meter of air (mg/m^3) divided by the percent SiO_2 2 averaged over an eight-hour work shift, and(for total dust) 30 mg/m^3 divided by the percent SiO_2 2 averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit changed to 50 micrograms respirable free silica per cubic meter of air (ug/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week. Uncontrolled abrasive blasting with silica sand presents such a severe silicosis hazard that NIOSH has recommended that silica sand, or other materials containing more than one percent free silica, be prohibited as an abrasive substance in abrasive blasting operations. The NIOSH Criteria Document for Crystalline Silica should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Crystalline silica can affect the body if it is inhaled.

- **Effects of overexposure**

Exposure to crystalline silica dust may cause scarring of the lungs with cough and shortness of breath. This is called "Silicosis."

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to crystalline silica.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to crystalline silica at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Crystalline silica causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Crystalline silica is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Crystalline silica or quartz dust causes silicosis, a form of disabling, progressive, and sometimes fatal pulmonary fibrosis characterized by the presence of typical nodulation in the lungs. The earliest lesions are seen in the region of the respiratory bronchioles. Lymphatics become obliterated by infiltration with dust-laden macrophages and granulation tissue. Morphologically, the typical lesion of silicosis is a firm nodule composed of concentrically arranged bundles of collagen. These nodules usually measure between 1 to 10 mm in diameter and appear around blood vessels and beneath the pleura, as well as in mediastinal lymph nodes. There

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may be conglomeration of nodules as the disease progresses, leading to massive fibrosis. Histologically, the silicotic nodule consists of a relatively acellular, avascular core of hyalinized reticulin fibers arranged concentrically and blending with collagen fibers toward the periphery, which has well-defined borders. The particles of silica responsible for the reaction are birefringent and can be visualized under polarized light if they exceed 1 micrometer in diameter. Silica in the lungs can be identified by x-ray diffraction studies and by incinerating a portion of the lung, with subsequent analysis of the ash. The silica content of the normal lung should not exceed 0.2% dry weight. The clinical signs and symptoms of silicosis tend to be progressive with continued exposure to quantities of dust containing free silica, with advancing age, and with continued smoking habits. Symptoms may also be exacerbated by pulmonary infections and cardiac decompensation. Symptoms include cough, dyspnea, wheezing, and repeated nonspecific chest illnesses. Impairment of pulmonary function may be progressive. In individual cases there may be little or no decrement when simple discrete nodular silicosis is present, but when nodulations become larger or when conglomeration occurs, recognizable cardiopulmonary impairment tends to occur. Progression of symptoms usually continues after dust exposure ceases. While there may be a factor of individual susceptibility to a given exposure to silica dust, the risk of onset and the rate of progression of the pulmonary lesion is clearly related to the character of the exposure (dust concentration and duration). The disease tends to occur after an exposure measured in years rather than months. Occasionally, exposures to very high concentrations occur in short periods of time in occupations such as sandblasters and tunnel workers; in these cases of acute or rapidly-developing silicosis there may be severe respiratory symptoms resulting in death. It is generally accepted that silicosis predisposes to active tuberculosis, and that the combined disease tends to be more rapidly progressive than uncomplicated silicosis. A group of 972 granite-shed workers was studied to relate exposure levels to incidence of silicosis. The workers were grouped according to average exposure levels: 3 - 9, 20, 27 - 44, 37-60 particles per cubic foot (mppcf). Those with the highest dust exposure showed development of early silicosis in 40% of the workers after 2 years and 100% after 4 years of exposure. The development of silicosis in the remaining workers appeared to be proportional to the dust exposure. At the second highest exposure level (27-44 mppcf), early stages of silicosis appeared after 4 years of exposure and more advanced stages developed by the seventh year. In the group exposed at an average of 20 mppcf there was little indication of severe effects upon the health of the workers. In the lowest exposure group, where the average dust concentration was 6 mppcf (range 3 to 9 mppcf), there was no indication of any untoward effects of dust exposure on workers.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 60.1
  2. Boiling point (760 mm Hg): 2230 C (4046 F)
  3. Specific gravity (water = 1): 2.2 – 3.0
  4. Vapor density (air = 1 at boiling point of crystalline silica): Not applicable
  5. Melting point: 1600 C (2912 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with powerful oxidizing agents such as fluorine, chlorine trifluoride, manganese trioxide, oxygen difluoride, etc. may cause fires.
  3. Hazardous decomposition products: None
  4. Special precautions: Crystalline silica is attacked by hydrogen fluoride (or hydrofluoric acid).
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant states that crystalline silica "has been observed to cause fibrotic nodules in the eye analogous to pulmonary silicosis. Particles of silica predominantly in the range of 2u to 3u introduced into the corneal stroma of rabbit eyes cause very little reaction. The same particles introduced into the anterior chamber sink to the bottom of the chamber and in the course of three to five weeks cause an inflammatory reaction with formation of fibrotic nodules in the iridocorneal angle. The reaction is quite different and more severe than that induced by brickdust, glass, or magnesium silicate . . . .

"An apparently unique report of involvement of the cornea in foundry workers who developed pulmonary silicosis has described gradual decrease in visual acuity due to corneal opacities in the pupillary area and has reported spectroscopic analytical evidence of an abnormally high silicon content in the cornea."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of crystalline silica on a filter, followed by an x-ray diffraction analysis. A detailed analytical method for diffraction analysis. An analytical method for crystalline silica is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to crystalline silica may occur and control methods which may be effective in each case:

Operation	Controls
Use in metallurgy industry for foundry molds, iron and steel castings, flux in smelting basic ores	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment
Use in manufacture of fiberglass for electrical insulation, chemical filtration, and reinforcing fabrics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from refining of sand for production of quartz	Process enclosure; local exhaust ventilation; water spray; personal protective equipment
Use in ceramics industry; use as an abrasive in scouring and polishing soaps and powders, flint sand paper, metal polishes, and sand blast work	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in processing synthetic quartz	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of refractories and building products; use in manufacture of electrical instruments for piezoelectric properties	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment
Use in grading and classification of electronic and optical grade quartz	Local exhaust ventilation; general dilution ventilation
Use in manufacture of optical equipment in prisms, wedges, and lenses	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment
Use in a variety of processes as paint extender, lining for acid towers, in the chemical industry in dental composition, in rocket engines and spacecraft, and graining lithographic plates	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during granite and similar material processing	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If crystalline silica dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of crystalline silica dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If crystalline silica is spilled or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Crystalline silica may be disposed of in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on crystalline silica, look up crystalline silica in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Crystalline Silica (November 1974)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Silica (Quartz)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR CRYSTALLINE SILICA

Condition	Minimum Respiratory Protection* Required Above X** mg/m^3
Particulate Concentration	
5X** mg/m^3 or less	Any dust respirator.
10X** mg/m^3 or less	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50X** mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500X** mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500X** mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**X indicates the permissible exposure as defined above.

Occupational Health Guideline for Silver Metal and Soluble Silver Compounds

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to metallic silver and all soluble silver compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Silver, metallic

- Formula: Ag
- Synonyms: None
- Appearance and odor: Characteristic white metallic solid with no odor.

Silver nitrate

- Formula: $AgNO_3$
- Synonyms: Argerol; lunar caustic
- Appearance and odor: Colorless and odorless solid which may become gray on storage.

Silver fluoride

- Formula: AgF
- Synonyms: None
- Appearance and odor: Yellow-white, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for silver metal and soluble silver compounds is 0.01 milligram of silver metal and soluble silver compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for silver metal and soluble silver compounds from 0.01 mg/m^3 to 0.1 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Silver or soluble silver compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Silver or soluble silver compounds can cause discoloration or blue-gray darkening of the eyes, nose, throat, and skin. Silver nitrate is strongly corrosive and can cause burns and permanent damage to the eyes and can burn the skin.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to silver metal or soluble silver compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to silver metal and soluble silver compounds at potentially hazardous levels:

1. Initial Medical Examination:

—Examination of the nasal septum, eyes, and skin for evidence of pigmentation: The purpose is to establish a baseline for future observations of silver deposition in tissues.

2. Periodic Medical Examination: The aforementioned

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The dust of silver and its soluble compounds cause argyria, the local or generalized impregnation of the mucous membranes, skin, and eyes with silver. Localized argyria occurs in the skin, eyes, nasal septum and throat, where gray-blue patches of pigmentation are formed without evidence of tissue reaction. Generalized argyria is recognized by the widespread pigmentation of the skin and may be seen first in the conjunctiva, with some localization in the inner canthus. Argyrosis of the respiratory tract has been described in two workers involved in the manufacture of silver nitrate; their only symptom was mild, chronic bronchitis; bronchoscopy revealed tracheobronchial pigmentation; biopsy of the nasal mucous membrane showed silver deposition in the subepithelial area. A total body burden from 1 to 5 g of silver will lead to generalized argyria. Silver, once deposited in the body, is poorly excreted in the urine in amounts detectable by spectrochemical methods. Silver nitrate (lunar caustic) may cause irritation, ulcers, and discoloration of skin; if ingested, it may cause abdominal pain and gastroenteritis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Silver, metallic**

1. Molecular weight: 107.9
2. Boiling point (760 mm Hg): 2200 C (3992 F)
3. Specific gravity (water = 1): 10.4
4. Vapor density (air = 1 at boiling point of metallic silver): Not applicable
5. Melting point: 966 C (1771 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Silver nitrate**

1. Molecular weight: 169.9
2. Boiling point (760 mm Hg): 444 C (831 F) (decomposes)
3. Specific gravity (water = 1): 4.4
4. Vapor density (air = 1 at boiling point of silver nitrate): Not applicable
5. Melting point: 209 C (408 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): 245
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Silver fluoride**

1. Molecular weight: 126.9
2. Boiling point (760 mm Hg): 1159 C (2119 F) (approximately)
3. Specific gravity (water = 1): 5.8
4. Vapor density (air = 1 at boiling point of silver fluoride): Not applicable
5. Melting point: 435 C (815 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): 64
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of metallic silver and soluble silver compounds with acetylene may cause formation of silver acetylide that is sensitive to shock. Contact with ammonia may cause formation of compounds that are explosive when dry. Contact with strong hydrogen peroxide solutions will cause violent decomposition to oxygen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when some soluble silver compounds decompose.
4. Special precautions: Soluble silver compounds will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Most soluble silver compounds are not combustible. However, silver nitrate is a strong oxidizing material capable of increasing the flammability of combustible, organic, or other readily oxidizable materials. The following soluble silver compounds are explosives and should be stored and handled in accordance with 29 CFR 1910.109: silver acetylide, silver azide, silver fulminate, silver oxalate mixtures, silver styphnate, silver tartarate mixtures, and silver tetrazene.

- **Warning properties**

According to Stecher "many silver salts are irritating . . to mucous membranes." Grant notes that many simple silver salts and silver ammonium compounds are injurious to the eye. According to Grant, "a great many reports have been published describing argyrosis of the eye, either from local contact with silver compounds or as a part of a generalized argyrosis from systemic absorption of silver or its compounds." Since there are inadequate data to assess the effects on the eye at or near the permissible exposure limit, for the purposes of this guideline, silver metal and soluble silver compounds are considered to have poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for silver metal and soluble silver compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with powdered metallic silver or solids or liquids containing soluble silver compounds, where skin contact may occur.
- If employees' clothing may have become contaminated with solids or liquids containing soluble silver compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with metallic silver or soluble silver compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substances from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the substances, the person performing the operation should be informed of substances' hazardous properties.
- Non-impervious clothing which becomes contaminated with metallic silver or soluble silver compounds should be removed promptly and not reworn until the metallic silver or soluble silver compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of powdered metallic silver or solids or liquids containing soluble silver compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to silver nitrate or solutions containing 5 percent or more silver nitrate by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with metallic silver or soluble silver compounds should be promptly washed or showered to remove any metallic silver or soluble silver compounds.
- Eating and smoking should not be permitted in areas where metallic silver or solids or liquids containing soluble silver compounds are handled, processed, or stored.
- Employees who handle powdered metallic silver or solids or liquids containing soluble silver compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to silver metal and soluble silver compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining and purification from ore; during refining from secondary sources	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of silver nitrate for use in photography, mirrors, plating, inks, dyes, and porcelain; and as germicides, antiseptics, caustics, and analytical reagents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of silver salts as catalysts in oxidation-reduction and polymerization reactions; in chemical synthesis; in glass manufacture, in silver-plating, in photography, as laboratory reagents, and in medicine	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Liberation from manufacture and casting of alloys; during fabrication of silver metal, alloys, and bi-metals for electrical uses; and during electroplating operations and fabrication of solders and brazing alloys; during manufacture and use of photographic chemicals and materials; during manufacture of mirrors, and during manufacture of silver powder pigments and paints	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of silver powder pigments and paints; during manufacture of mirrors; during manufacture of photographic chemicals and materials	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If powdered metallic silver or solids or liquids containing soluble silver compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If powdered metallic silver or solids or liquids containing soluble silver compounds get on the skin, flush the contaminated skin with water. If powdered metallic silver or solids or liquids containing soluble silver compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention. Other silver compounds should be removed by promptly flushing the skin with water.

- **Breathing**

If a person breathes in large amounts of silver metal or soluble silver compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If silver nitrate or other corrosive soluble silver compounds have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the silver nitrate or other corrosive silver compounds. Do not attempt to make the exposed person vomit. Get medical attention immediately. When non-corrosive soluble silver compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If powdered silver metal or soluble silver compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing silver metal or soluble silver compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Silver metal and soluble silver compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR SILVER METAL AND SOLUBLE SILVER COMPOUNDS

Condition	**Minimum Respiratory Protection* Required Above 0.01 mg/m^3**
Particulate Concentration	
0.5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
20 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soapstone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $3\ MgO\text{-}4SiO_2\text{-}H_2O$
- Synonyms: Massive talc; steatite
- Appearance and odor: Slippery solid with no odor. (Soapstone contains less than 10% tremolite and less than 1% crystalline silica).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soapstone is 20 million particles of soapstone per cubic foot of air (mppcf) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soapstone can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to soapstone may cause scarring of the lungs. Shortness of breath, cough, enlargement of the ends of the fingers and heart failure may occur with this condition. Workers exposed to soapstone have been found to have an increased amount of cancer of the lungs and pleura.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soapstone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soapstone at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Soapstone contains fibrous talc which can cause pneumoconiosis and lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Soapstone contains fibrous talc which is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Soapstone dust contains varying percentages of fibrous talc, which causes fibrotic pneumoconiosis and an increased incidence of cancer of the lungs and pleura. In the development of talc pneumoconiosis or talcosis, the subject initially is symptom-free, but cough and dyspnea develop as the disease progresses; cyanosis, digital clubbing, and cor pulmonale occur in advanced cases. The disease progresses slowly, even in the absence of continued exposure; occasionally, the disease may progress rapidly, with death occurring within a few years of a very heavy exposure. In an epidemiologic study of 260 workers with 15 or more years of exposure to commercial talc dust containing talc, tremolite, anthophyllite, carbonate dusts, and a small amount of free silica, the mortality rate from cancer of the lungs and pleura was four times greater than expected; in addition, a major cause of death among these workers was cor pulmonale, a result of the pneumoconiosis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Formula weight: 379.2
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.7 – 2.8
4. Vapor density (air = 1 at boiling point of soapstone): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

According to the *Documentation of TLV's*, "soapstone does not have a precise mineralogic connotation. Many rocks of variable composition are sometimes so designated. Massive talc is sometimes called soapstone or steatite. The terms are not synonymous, and some forms of soapstone have as little as 50% talc." Grant states that "talc employed in fulling of cloth is said to have caused conjunctival inflammation resulting in symblepharon, severe enough to require surgery in some instances."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for soapstone had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soapstone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, quarrying, and blasting of soapstone	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of acid-proof coverings in floors, tables, sinks, etc.; use in switch-board panels for high electrical resistance; use in Kraft process of pulp manufacture; use in fume cupboards and fireless cookers; use in crayons for marking cloth, metal, and glass	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If soapstone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soapstone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Under-

stand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If hazardous amounts of soapstone are spilled or released, the following steps should be taken:

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Soapstone may be disposed of in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOAPSTONE

Condition	Minimum Respiratory Protection* Required Above 20 mppcf
Particulate Concentration	
100 mppcf or less	Any dust respirator.
200 mppcf or less	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
1000 mppcf or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 mppcf or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
Greater than 10,000 mppcf or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Fluoride Dust (as Fluoride)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all fluoride. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Sodium fluoride

- Formula: NaF
- Synonyms: None
- Appearance and odor: Colorless or blue, odorless solid.

Cryolite (sodium hexafluoroaluminate)

- Formula: Na_3AlF_6
- Synonyms: Sodium hexafluoroaluminate
- Appearance and odor: Colorless to dark, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluoride is 2.5 milligrams of fluoride per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to 2.5 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Inorganic Fluorides should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Fluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Fluoride containing dust may cause irritation of the eyes and respiratory tract. Swallowing fluoride may cause a salty or soapy taste, vomiting, abdominal pain, diarrhea, shortness of breath, difficulty in speaking, thirst, weakness of the pulse, disturbed color vision, muscular weakness, convulsions, loss of consciousness, and death. Kidney injury and bleeding from the stomach may occur.

2. Long-term Exposure: Repeated exposure to fluoride containing dust may cause excessive calcification of the bone and calcification of ligaments of the ribs, pelvis, and spinal column. Stiffness and limitation of motion may result. Repeated or prolonged exposure of the skin to fluoride containing dust may cause a skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to fluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, central nervous system, skeletal system, and the kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney disease interferes with excretion of fluoride, thus increasing the risk from exposure to excessive fluoride, a urinalysis should be

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obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic examination on centrifuged sediment. An analysis for fluoride should be performed.

—Pelvic roentgenogram: Fluoride causes skeletal abnormalities. A radiologic examination of the male pelvis with proper gonadal shielding should be conducted at the time of the preplacement examination and when indicated by analysis of the results of the urinary fluoride tests.

—Eye disease: Fluoride is an eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Fluoride may cause respiratory system effects, such as fibrosis and asthma. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Fluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Fluoride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that the radiologic examination of the pelvis should be conducted only when clinically indicated.

- **Summary of toxicology**

Fluoride causes irritation of the eyes and respiratory tract; absorption of excessive amounts of fluoride over a long period of time results in increased radiographic density of bone. The lethal oral dose of sodium fluoride for humans is approximately 5 g; effects are diffuse abdominal pain, diarrhea, and vomiting; excessive salivation, thirst, and perspiration; painful spasms of the limbs; and sometimes albuminuria. Workers exposed to an airborne fluoride concentration of 5 mg/m^3 complained of eye and respiratory tract irritation and nausea. A portion of absorbed fluoride is stored in bone and part is excreted promptly in the urine; with continued exposure and increasing amounts of fluoride already present in the bone, the fraction appearing in the urine increases. Some storage of fluoride occurs from the ingestion of as little as 3 mg/day. Repeated exposure to excessive concentrations of fluorides over a period of years results in increased radiographic density of bone and eventually may cause crippling fluorosis (osteosclerosis due to deposition of fluoride). The gross changes in the skeleton are quite distinctive and characteristic; as the amount of fluoride in the bone increases, exostoses may develop, especially on the long bones; the spinal and pelvic ligaments begin to calcify, occasionally vertebrae fuse together, and a typical stiffness of the spinal column develops. The absorption of 20 to 80 mg of fluoride daily may be expected to lead to crippling fluorosis in 10 to 20 years; this condition has not been reported in the United States from industrial exposure. Evidence from several sources indicates that urinary fluoride concentrations not exceeding 5 mg/l in preshift samples taken after 2 days off work are not associated with detectable osteosclerosis and that such changes are unlikely at urinary levels of 5 to 8 mg/l. Repeated or prolonged exposure of the skin to fluoride-bearing dusts and fumes may cause dermatitis. Mottled appearance and altered form of teeth are most pronounced when excessive amounts of fluoride are ingested during the period of formation and calcification of teeth, which occurs during the first 8 years of life in humans; after the teeth erupt and calcification has been completed, fluoride does not have an adverse effect on the teeth.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Sodium fluoride**

1. Molecular weight: 42
2. Boiling point (760 mm Hg): 1702 C (3095 F)
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of sodium fluoride): Not applicable
5. Melting point: 992 C (1818 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 4.2
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cryolite (sodium hexafluoroaluminate)**

1. Molecular weight: 209.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of cryolite): Not applicable
5. Melting point: 1009 C (1848 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.04
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong acids may cause formation of toxic and irritating hydrogen fluoride gas.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Concerning fluorides, Grant states that "industrially, fluorides may contact the eyes in the form of fumes from fluxes in soldering, in welding, and in magnesium foundries. Irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m^3 of air."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of fluoride in an impinger containing sodium hydroxide, followed by dilution with a buffer, and analysis with an ion-specific electrode. An analytical method for fluoride is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with fluoride.
- If employees' clothing has had any possibility of being contaminated with fluoride, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with fluoride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of fluoride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the fluoride, the person performing the operation should be informed of fluoride's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of sodium fluoride or liquids containing sodium fluoride contacting the eyes.
- Non-impervious clothing which becomes contaminated with fluoride should be removed promptly and not reworn until the fluoride is removed from the clothing.

SANITATION

- Skin that becomes contaminated with fluoride should be promptly washed or showered to remove any fluoride.
- Eating and smoking should not be permitted in areas where fluoride is handled, processed, or stored.
- Employees who handle fluoride should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to fluoride dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, benefication, packaging, and distribution of fluorspar	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from fluorides from phosphate rock treatment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from use of fluorspars as a fluxing additive for steel production	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from manufacture of cryolite from phosphate rock processing; use of fluorspar and cryolite in the production of metallic aluminum by electrolysis	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in formulations of insecticides for agricultural crops, fruits, vegetables, ornamentals, and trees	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in chemical industry as a source of fluorine compounds; use of fluorspar and cryolite in ceramics and glass industry in manufacture of fiberglass, optical glass, lenses, and pottery; use of fluorspar in manufacture of welding rods and welding fluxes; use in electroplating	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in treatment of water	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If fluoride or liquids containing fluoride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If fluoride or liquids containing fluoride get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If fluoride or liquids containing fluoride soak through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of fluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquids containing fluoride have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.
- If fluoride is spilled or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing fluoride should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Fluoride may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR FLUORIDE DUST (AS FLUORIDE)

Condition	**Minimum Respiratory Protection*** **Required Above 2.5 mg/m³**
Particulate Concentration	
12.5 mg/m³ or less**	A single-use dust respirator.
25 mg/m³ or less**	Any dust respirator, except single-use or quarter-mask respirator.*** Any supplied-air respirator. Any self-contained breathing apparatus.
125 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece.*** Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter, and a full facepiece.*** A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 250 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	An escape gas mask with an acid gas canister. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***If acid gases are present, air-purifying elements providing protection against acid gases and including the indicated filters should be used.

Occupational Health Guideline for Sodium Fluoroacetate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_2FCOONa$
- Synonyms: 1080; sodium monofluoroacetate; SFA
- Appearance and odor: Fluffy, white, odorless hygroscopic solid (sometimes dyed black).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sodium fluoroacetate is 0.05 milligram of sodium fluoroacetate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sodium fluoroacetate can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Sodium fluoroacetate may cause vomiting, apprehension, hallucinations, tingling of the nose and face, numbness of the face and facial twitching. It may also cause excitation and convulsions. Depression may occur after and between convulsive episodes. The heart may beat irregularly or stop. Symptoms are often delayed 30 minutes to two hours after swallowing this chemical.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sodium fluoroacetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sodium fluoroacetate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders or cardiovascular disease would be expected to be at increased risk from exposures. Examination of the nervous system, heart, lungs, and kidneys should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to sodium fluoroacetate, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—An electrocardiogram: Sodium fluoroacetate causes cardiac arrhythmias. Periodic surveillance of the heart is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Sodium fluoroacetate as the dust or in solution is highly toxic and causes convulsions and ventricular fibrillation. Fluoroacetate is metabolized to fluorocitrate, which blocks the tricarboxylic acid cycle, an essential element of energy production in mammalian cells. Estimates of the lethal oral dose in humans range from 2 to 10 mg/kg. Onset of symptoms after ingestion is frequently delayed for 30 minutes to 2 hours; effects are vomiting, apprehension, auditory hallucinations, nystagmus, tingling sensation of nose, numbness of face, facial twitching, and epileptiform convulsions. After a period of several hours there may be pulsus alternans, long sequences of ectopic heartbeats (often multifocal), tachycardia, ventricular fibrillation, and death. In a fatal

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case of ingestion, autopsy findings included hemorrhagic pulmonary edema and degeneration of renal tubules.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of sodium fluoroacetate): Not applicable
5. Melting point: 200 C (392 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 111
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: None.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and carbon monoxide) may be released when sodium fluoroacetate decomposes.
4. Special precautions: None.

- **Flammability**

1. Not combustible

- **Warning properties**

Sodium fluoroacetate is not known to be an eye irritant. Grant describes some effects on the eye caused by this compound, but these are systemic effects.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for sodium fluoroacetate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with sodium fluoroacetate or solutions containing sodium fluoroacetate.
- If employees' clothing has had any possibility of being contaminated with sodium fluoroacetate or solutions containing sodium fluoroacetate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with sodium fluoroacetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sodium fluoroacetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sodium fluoroacetate, the person performing the operation should be informed of sodium fluoroacetate's hazardous properties.
- Where there is any possibility of exposure of an employee's body to sodium fluoroacetate or solutions containing sodium fluoroacetate, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with sodium fluoroacetate should be removed immediately and not reworn until the sodium fluoroacetate is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium fluoroacetate or solutions containing sodium fluoroacetate may contact the eyes.

SANITATION

- Skin that becomes contaminated with sodium fluoroacetate should be immediately washed or showered to remove any sodium fluoroacetate.
- Workers subject to skin contact with sodium fluoroacetate or solutions containing sodium fluoroacetate should wash any areas of the body which may have contacted sodium fluoroacetate at the end of each work

day.

- Eating and smoking should not be permitted in areas where sodium fluoroacetate or solutions containing sodium fluoroacetate are handled, processed, or stored.
- Employees who handle sodium fluoroacetate or solutions containing sodium fluoroacetate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sodium fluoroacetate may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticides	Local exhaust ventilation; personal protective equipment
Use in hand or aircraft application for pest control	Personal protective equipment; material substitution (product replacement)
Manufacture of sodium fluoroacetate	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If sodium fluoroacetate or solutions containing sodium fluoroacetate get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If sodium fluoroacetate or solutions containing sodium fluoroacetate get on the skin, immediately flush the contaminated skin with water. If sodium fluoroacetate or solutions containing sodium fluoroacetate penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation is present after washing, get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of sodium fluoroacetate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When sodium fluoroacetate or solutions containing sodium fluoroacetate have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If sodium fluoroacetate is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing sodium fluoroacetate should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Sodium fluoroacetate may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SODIUM FLUOROACETATE

Condition	**Minimum Respiratory Protection*** **Required Above 0.05 mg/m^3**
Particulate Concentration	
0.25 mg/m^3 or less	Any dust and mist respirator, except single-use.
0.5 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
2.5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Sodium Hydroxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: NaOH
- Synonyms: Caustic soda, soda lye, lye
- Appearance and odor: White, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sodium hydroxide is 2 milligrams of sodium hydroxide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 2 mg/m^3 over a 15-minute period. The NIOSH Criteria Document for Sodium Hydroxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sodium hydroxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Sodium hydroxide is a strong alkali and is corrosive to any tissue with which it comes in contact. Effects from inhalation of the dusts and mists will vary from mild irritation to destructive burns depending on the severity of exposure. Severe pneumonitis may occur. Sodium hydroxide as a solid or in dusts, mists or solutions may cause irritation of the eyes and, with greater exposure, severe burns with possible blindness. Contact of the skin with sodium hydroxide as a solid or in dusts, mists or solutions may cause skin irritation and, with greater exposure, severe burns with scarring. Swallowing solid sodium hydroxide or solutions of sodium hydroxide may cause severe burns of the mouth, throat, and stomach. Death may result. Severe scarring of the throat may occur on recovery after swallowing sodium hydroxide. An increased number of esophageal cancer cases have been reported to occur in individuals who have scarring of the esophagus from swallowing sodium hydroxide.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sodium hydroxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sodium hydroxide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sodium hydroxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sodium hydroxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Sodium hydroxide is a strong alkali; the mist, dust and solutions cause severe injury to the eyes, mucous mem-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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branes, and skin. Although inhalation is usually of secondary importance in industrial exposures, the effects from the dust or mist will vary from mild irritation of the nose at 2 mg/m^3 to severe pneumonitis, depending on the severity of exposure. The greatest industrial hazard is rapid tissue destruction of eyes or skin upon contact with either the solid or with concentrated solutions. Contact with the eyes causes disintegration and sloughing of conjunctival and corneal epithelium, corneal opacification, marked edema, and ulceration; after 7 to 13 days either gradual recovery begins, or there is progression of ulceration and corneal opacification. Complications of severe eye burns are symblepharon (adhesion of the lid to the eyeball) with overgrowth of the cornea by a vascularized membrane, progressive or recurrent corneal ulceration, and permanent corneal opacification. On the skin, solutions of 25 to 50% cause the sensation of irritation within about 3 minutes; with solutions of 4%, this does not occur until after several hours. If not removed from the skin, severe burns with deep ulceration will occur; exposure to the dust or mist may cause multiple small burns, with temporary loss of hair. Ingestion produces severe pain in the esophagus and stomach, corrosion of the lips, mouth, tongue, and pharynx and the vomiting of large pieces of mucosa; cases of squamous cell carcinoma of the esophagus have occurred with latent periods of 12 to 42 years after ingestion; these cancers may have been sequelae of tissue destruction and possibly scar formation rather than from a direct carcinogenic action of sodium hydroxide itself.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 40
  2. Boiling point (760 mm Hg): 1390 C (2534 F)
  3. Specific gravity (water = 1): 2.13
  4. Vapor density (air = 1 at boiling point of sodium hydroxide): Not applicable
  5. Melting point: 310 C (590 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 50
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with water, acids, flammable liquids, and organic halogen compounds, especially trichloroethylene, may cause fires and explosions. Contact with metals such as aluminum, tin, and zinc causes formation of flammable hydrogen gas. Contact with nitromethane and other similar nitro compounds causes formation of shock-sensitive salts.
  3. Hazardous decomposition products: None
  4. Special precautions: Sodium hydroxide will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant states that sodium hydroxide "is severely injurious to all tissues, and causes some of the most severe injuries of the eye. The serious problem presented by sodium hydroxide and other alkalies which cause devastating injuries of the eye have been succinctly and well described by Stanley, emphasizing particularly the dangers of caustic household drain cleaners that contain sodium hydroxide.

"The effects of splashes of sodium hydroxide on the eyes of human beings have been described innumerable times . . . . Damage of the cornea, conjunctiva, and episcleral tissues is usual, but damage of intraocular structures is relatively rare."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of sodium hydroxide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of sodium hydroxide in a glass bubbler containing hydrochloric acid, followed by subsequent titration. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sodium hydroxide may be used. An analytical method for sodium hydroxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with sodium hydroxide or solutions of sodium hydroxide.
- If employees' clothing may have become contaminated with solid sodium hydroxide, employees should change into uncontaminated clothing before leaving the work premises.
- Where there is any possibility of exposure of an employee's body to sodium hydroxide or solutions of sodium hydroxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with sodium hydroxide should be removed immediately and not reworn until the sodium hydroxide is removed from the clothing.
- Clothing contaminated with sodium hydroxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sodium hydroxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sodium hydroxide, the person performing the operation should be informed of sodium hydroxide's hazardous properties.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of sodium hydroxide or solutions of sodium hydroxide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to sodium hydroxide or solutions of sodium hydroxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with sodium hydroxide should be immediately washed or showered to remove any sodium hydroxide.
- Eating and smoking should not be permitted in areas where sodium hydroxide or solutions containing sodium hydroxide are stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sodium hydroxide may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical manufacture; explosives manufacture; use in boiler water and as a laboratory reagent; use in pH control in textiles, paper, and chemical industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of synthetic fibers and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of pulp and paper; in pulping Kraft process; manufacture of insulating board	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metal processing and refining; use in petroleum refining for removal of sulfur compounds; as a flotation reagent; as a modifier and slime depressant; in pH control	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of soaps and detergents; as a saponifying agent; use in metal cleaning; in laundering, bleaching, and dishwashing; use in drain cleaners and oven cleaners	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in food processing to peel fruits and vegetables, process olives, and refine vegetable oils	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Use in glass manufacture as a source of sodium oxide	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If sodium hydroxide, as a solid or in dusts, mists, or solutions, get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If sodium hydroxide, as a solid or in dusts, mists, or solutions, gets on the skin, immediately flush the contaminated skin with water. If sodium hydroxide, as a solid or in dusts, mists, or solutions, penetrates through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of sodium hydroxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If solutions of sodium hydroxide have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sodium hydroxide. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If sodium hydroxide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Dilute with water and neutralize with 6 molar hydrochloric acid.

- Waste disposal method:

Sodium hydroxide may be disposed of in sealed containers in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on sodium hydroxide, look up sodium hydroxide in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Sodium Hydroxide (September 1975)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Sodium Hydroxide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- von Oettingen, W. F.: *Poisoning: A Guide to Clinical Diagnosis and Treatment* (2nd ed.), Saunders, Philadelphia, 1958.

RESPIRATORY PROTECTION FOR SODIUM HYDROXIDE

Condition	Minimum Respiratory Protection* Required Above 2 mg/m³
Particulate Concentration	
100 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator with a full facepiece, except single-use. Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of sodium hydroxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Stibine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: SbH_3
- Synonyms: Hydrogen antimonide; antimony trihydride
- Appearance and odor: Colorless gas with a disagreeable odor like hydrogen sulfide.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for stibine is 0.1 part of stibine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.5 milligram of stibine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Stibine can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Stibine may cause destruction of the red blood cells with headache, nausea, weakness, and back and abdominal pain. It may later cause dark red urine, yellow jaundice, kidney damage, and death. It may also cause lung irritation.

2. Long-term Exposure: Not known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to stibine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to stibine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, liver, and kidneys should be stressed.

—A complete blood count: Stibine causes red blood cell hemolysis. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage has been observed in humans exposed to stibine, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to stibine, a profile of liver function should be performed by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Stibine gas is an extremely toxic hemolytic agent which causes injury to the liver and kidneys; it also may be a lung irritant. Guinea pigs exposed to 65 ppm for 1 hour developed hemoglobinuria, followed within a few days by profound anemia. Cats and dogs exposed to 40-45 ppm for 1 hour developed pulmonary edema, and some died within 24 hours. Acute exposures to humans would be expected to cause rapid destruction of red blood cells, hemoglobinuria, anuria, jaundice, and death. Workers exposed to a mixture of gases of stibine, arsine, and hydrogen sulfide developed headache, weakness, nausea, abdominal and lumbar pain, hematuria, and profound anemia.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 124.8
2. Boiling point (760 mm Hg): −17 C (1 F)
3. Specific gravity (water = 1): Liquid = 2.2 at boiling point
4. Vapor density (air = 1 at boiling point of stibine): 4.34
5. Melting point: −88 C (−126 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Stibine reacts with acids, halogenated hydrocarbons, oxidizers, and moisture.
3. Hazardous decomposition products: Antimony and hydrogen will be released when stibine dcomposes.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: Patty states that "stibine has an extremely unpleasant odor that can serve as a warning; whether the threshold of odor detection is sufficiently low to prevent injury is uncertain." No quantitative information is available concerning the odor threshold of stibine.
2. Eye Irritation Level: Stibine is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of stibine, this gas is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of stibine on mercuric chloride-impregnated silica gel, followed by extraction with concentrated hydrochloric acid, and colorimetric analysis. An analytical method for stibine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to stibine may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from treatment of scum formed on surface of molten metals treated with acid	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during charging as storage batteries	Local exhaust ventilation; general dilution ventilation
Liberation from alloys of antimony compounds which come in contact with reducing acids	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation from purification of antimony by electrolysis	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a chemical intermediate and in chemical synthesis	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of stibine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If stibine is leaked or released, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Control source of stibine formation.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Stibine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Stibine," *Hygienic Guide Series*, Detroit, Michigan, 1960.
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- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

RESPIRATORY PROTECTION FOR STIBINE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against stibine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Stoddard Solvent

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Generally C_9 through C_{11} paraffins (85%) and aromatics (15%)
- Synonyms: Dry cleaning safety solvent; mineral spirits
- Appearance and odor: Colorless liquid with kerosene-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Stoddard solvent is 500 parts of Stoddard solvent per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2950 milligrams of Stoddard solvent per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit for refined petroleum products, including Stoddard solvent, be reduced to 350 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 1800 mg/m^3 measured over a 15-minute period. The NIOSH Criteria Document for Refined Petroleum Products should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Stoddard solvent can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to Stoddard solvent causes irritation of the eyes, nose, and throat, and may cause dizziness. Very high air concentrations may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure to the liquid may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Stoddard solvent.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Stoddard solvent at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, blood, urine, and central nervous system should be stressed.

—Skin: Stoddard solvent is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver function tests: Stoddard Solvent may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Urinalysis: The kidneys may be affected by Stoddard solvent. Since kidney damage has been observed from exposure, a urinalysis should be performed to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—A complete blood count: A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Respiratory system examination: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Stoddard solvent might cause exacerbation of symptoms due to its irritant properties.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, tney may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. *Periodic Medical Examination:*The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Stoddard solvent vapor is a mild narcotic and a mucous membrane irritant. Since it contains both aliphatic and aromatic hydrocarbons in varying concentrations, toxicologic opinion is based upon deductions as to the relative health hazard of the different fractions. The vapor of the aliphatic fractions is chiefly nonane and isodecane. The aromatic component is considered to be more toxic. Stoddard solvent has an odor threshold of about 4 to 5 mg/m^3 and olfactory fatigue has been observed in about 6 minutes at low concentrations. Eye irritation was reported in a test exposure of human subjects at 850 mg/m^3. Industrial exposures to unknown but fairly high concentrations over long periods have resulted in headaches, eye, nose, and throat irritation, fatigue, marrow hypoplasia and, in extreme cases, death. Dermal exposures to the liquid solvent have caused dermatitis and jaundice.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 144 (approximately)
2. Boiling point (760 mm Hg): 150 to 200 C (302 to 392 F)
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of Stoddard solvent): 5
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 2 mm Hg (estimate)
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving Stoddard solvent.
4. Special precautions: Stoddard solvent will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 38.7 to 60 C (102 to 140 F) (closed cup)
2. Autoignition temperature: 226 to 260 C (440 to 500 F)
3. Flammable limits in air, % by volume: Lower: 0.8
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: May gives an odor threshold of 30 ppm for Stoddard solvent (mineral spirits). According to the AIHA *Hygienic Guide* for Stoddard solvent, "most Stoddard solvents have a petroleum odor that is perceptible at about 1 ppm."
2. Eye Irritation Level: Grant states that "the vapor of Stoddard solvent is perceptively irritating to human eyes at 400 ppm."
3. Evaluation of Warning Properties: Through its odor and irritant effects, Stoddard solvent can be detected below the permissible exposure limit. For the purposes of this guideline, therefore, Stoddard solvent is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of Stoddard solvent. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of Stoddard solvent vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure Stoddard solvent may be used. An analytical method for Stoddard solvent is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid Stoddard solvent.
- Clothing wet with liquid Stoddard solvent should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of Stoddard solvent from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the Stoddard solvent, the person performing the operation should be informed of Stoddard solvent's hazardous properties.
- Any clothing which becomes wet with liquid Stoddard solvent should be removed promptly and not reworn until the Stoddard solvent is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid Stoddard solvent may contact the eyes.

SANITATION

- Skin that becomes wet with liquid Stoddard solvent should be promptly washed or showered with soap or mild detergent and water to remove any Stoddard solvent.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Stoddard solvent may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in dry cleaning industry	Process enclosure; local exhaust ventilation; personal protective equipment
Use in paint and varnish industries	General dilution ventilation
Use as a solvent for printing inks and textile-printing industries	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of aerosol sprays as a solvent for paints, varnishes, and insecticides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of sprays for pesticides, herbicides, household cleaners, and silicone compounds	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent and thinner in protective coating materials	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in metal cleaning and degreasing; and in leather degreasing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a general solvent in fabric waterproofing, processing of synthetic yarns, extraction of fats and oils, as a tackifying agent for rubber, in rubber cements, and in polishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If Stoddard solvent gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If Stoddard solvent gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If Stoddard solvent soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of Stoddard solvent, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If Stoddard solvent has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If Stoddard solvent is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Stoddard solvent should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Stoddard solvent may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Stoddard Solvent," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR STODDARD SOLVENT

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Strychnine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{21}H_{22}N_2O_2$
- Synonyms: None
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for strychnine is 0.15 milligram of strychnine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Strychnine affects the body after it is swallowed. There are no literature sources to indicate that strychnine presents a significant hazard from skin or eye exposure.

- **Effects of overexposure**

After swallowing strychnine, effects usually occur within 10 to 30 minutes and include stiffness of the face and neck muscles, increased excitability, restlessness, and apprehension. These symptoms may progress to repeated convulsions and death.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to strychnine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to strychnine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from strychnine exposure.

—Convulsive disorders: Strychnine causes convulsions. Persons with a history of convulsive disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Strychnine is a potent convulsant. In humans the mean lethal oral dose is approximately 100 to 120 mg. After ingestion, effects usually occur within 10 to 30 minutes and include stiffness of the face and neck muscles, increased reflex excitability, restlessness, apprehension, and heightened acuity of perception. Any sensory stimulus may produce a violent motor response which in the early stages of intoxication tends to be a coordinated extensor thrust and in later stages it may be a tetanic convulsion with opisthotonos; anoxia and cyanosis develop rapidly. Between convulsions, muscular relaxation is complete, breathing is resumed, and cyanosis lessens. Because sensation is unaffected, the convulsions are painful and lead to overwhelming fear; as many as 10 convulsions separated by intervals of 10 to 15 minutes may be experienced, but death often occurs after the second to fifth convulsion and even the first convulsion may be fatal if sustained; death is commonly due to asphyxia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 334.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.36
4. Vapor density (air = 1 at boiling point of strychnine): Not applicable
5. Melting point: 268 C (547 F)
6. Vapor pressure at 20 C (68 F): Essentially zero

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7. Solubility in water, g/100 g water at 20 C (68 F): 0.02

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released when strychnine decomposes.
4. Special precautions: None.

- **Flammability**

1. Not combustible

- **Warning properties**

Strychnine is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for strychnine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- If employees' clothing has had any possibility of being contaminated with strychnine or liquids containing strychnine, employees should change into uncontaminated clothing before leaving the work premises.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with strychnine where skin contact may occur.
- Clothing which has had any possibility of being contaminated with strychnine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of strychnine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the strychnine, the person performing the operation should be informed of strychnine's hazardous properties.

SANITATION

- Eating and smoking should not be permitted in areas where strychnine or liquids containing strychnine are handled, processed, or stored.
- Skin that becomes contaminated with strychnine or liquids containing strychnine should be promptly washed or showered to remove any strychnine.
- Employees who handle strychnine or liquids containing strychnine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to strychnine may occur and control methods which may be effective in each case:

Operation	Controls
Application and formulation of medicinals and pesticides	Personal protective equipment
Manufacture of strychnine	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If strychnine or liquids containing strychnine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If strychnine or liquids containing strychnine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If strychnine or liquids containing strychnine penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of strychnine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When strychnine or liquids containing strychnine have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If strychnine is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing strychnine should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Strychnine may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Strychine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR STRYCHNINE

Condition	**Minimum Respiratory Protection*** **Required Above 0.15 mg/m³**
Particulate Concentration	
0.75 mg/m³ or less	Any dust respirator, except single-use.
1.5 mg/m³ or less	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
3 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. A powered air-purifying respirator with a high efficiency particulate filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 3 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Styrene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5CH=CH_2$
- Synonyms: Phenylethylene; vinylbenzene; cinnamene; styrene monomer
- Appearance and odor: Colorless liquid with a sweet aromatic odor at low concentrations. Sharp, penetrating, and disagreeable odor at higher concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for styrene is 100 parts of styrene per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and an acceptable peak of 600 ppm for 5 minutes in any three-hour period. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for styrene from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Styrene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Styrene may irritate the eyes, nose, throat, and skin. High concentrations may cause a person to become sleepy or to become unconscious.

2. Long-term Exposure: Repeated skin contact with styrene may produce a skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to styrene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to styrene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from styrene exposure.

—Central nervous system disorders: Since exposure to styrene vapor or liquid on the skin has been observed to result in central nervous system depression and occasional abnormalities in the electroencephalogram, persons with pre-existing disorders may be unusually susceptible to these effects.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of styrene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Skin disease: Styrene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although styrene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although styrene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Exposure to concentrations of styrene above 200 ppm

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causes irritation of the eyes and upper respiratory tract. There is cracking and inflammation of the skin due to defatting. Higher exposures depress the central nervous system. Electroencephalographic changes have been reported. Styrene is excreted fairly rapidly in the urine, largely as hippuric acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 104
2. Boiling point (760 mm Hg): 145 C (293 F)
3. Specific gravity (water = 1): 0.90
4. Vapor density (air = 1 at boiling point of styrene): 3.6
5. Melting point: −30.6 C (−23 F)
6. Vapor pressure at 20 C (68 F): 4.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
8. Evaporation rate (butyl acetate = 1): 0.49

- **Reactivity**

1. Conditions contributing to instability: Styrene is stabilized by a polymerization inhibitor (often tert-butylcatechol). If this is not present in adequate concentrations, styrene can polymerize and explode its container. The polymerization is also speeded up by temperatures above 66 C (150 F).
2. Incompatibilities: Avoid contact with oxidizing agents and catalysts for vinyl polymerization, such as peroxides, strong acids, and aluminum chloride.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving styrene. Styrene fumes are very acrid.
4. Special precautions: Styrene will corrode copper and copper alloys and dissolve rubber.

- **Flammability**

1. Flash point: 32 C (90 F) (closed cup)
2. Autoignition temperature: 490 C (914 F)
3. Flammable limits in air, % by volume: Lower: 1.1; Upper: 6.1
4. Extinguishant: Dry cemical, foam, or carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports that the odor threshold of styrene is 0.08 ppm.
2. Eye Irritation Level: The AIHA *Hygienic Guide* reports that "styrene vapor at concentrations of 200 to 400 ppm was found to have transient irritant effects on the eyes."

4\. Evaluation of Warning Properties: Since the odor threshold of styrene is below the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of styrene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of styrene. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of styrene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure styrene may be used. An analytical method for styrene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National

Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid styrene.
- Clothing wet with liquid styrene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of styrene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the styrene, the person performing the operation should be informed of styrene's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid styrene should be removed promptly and not reworn until the styrene is removed from the clothing.
- Any clothing which becomes wet with liquid styrene should be removed immediately and not reworn until the styrene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid styrene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid styrene should be promptly washed or showered with soap or mild detergent and water to remove any styrene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to styrene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray-up manufacture of glass fiber, reinforced styrene-polyester articles	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during spray application of styrene polyester surface coatings	Process enclosure; local exhaust ventilation; personal protective equipment
Use during hand lay-up of glass fibers, reinforced styrene-polyester articles	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during molding of articles or potting electrical components with polystyrene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of tires and other rubber goods using styrene-butadiene elastomers (SBR)	General dilution ventilation
Use in manufacture of concretes	General dilution ventilation; personal protective equipment
Use during bag lay-up manufacture of glass fiber, reinforced styrene-polyester articles; during use of surface coatings containing styrene-butadiene copolymer resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during die molding of articles made from styrene-polyester resins; during brush application of surface coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in process operations for production of polystyrene, acrylonitrile-butadiene styrene (ABS), styrene-acrylonitrile (SAN), and styrene-butadiene copolymers	Local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings; use in miscellaneous processes as an elastomer, intermediate, or starting material; use during manufacture of ion-exchange resins (styrene-divinylbenzene copolymer)	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If styrene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If styrene gets on the skin, promptly flush the contaminated skin with water. If styrene soaks through the clothing, remove the clothing immediately and flush the skin with water When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of styrene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If styrene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If styrene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

- Waste disposal methods:

Styrene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

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RESPIRATORY PROTECTION FOR STYRENE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
400 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Sulfur Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: SO_2
- Synonyms: None
- Appearance and odor: Colorless gas with a characteristic pungent odor. It can be a liquid at temperatures below −10 C (14 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfur dioxide is 5 parts of sulfur dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 13 milligrams of sulfur dioxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 0.5 ppm as a time-weighted average for up to a 10-hour work shift, 40-hour work week. For more detailed information, the NIOSH Criteria Document for Sulfur Dioxide and the NIOSH testimony presented at the Department of Labor's Public Hearing on a Proposed Standard for Sulfur Dioxide should be consulted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfur dioxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Sulfur dioxide gas is intensely irritating to the eyes and respiratory tract causing burning of the eyes and tearing, coughing, and chest tightness. It may cause severe breathing difficulties. Severe exposures to sulfur dioxide may cause a person to stop breathing. Liquid sulfur dioxide may cause eye burns with loss of vision and skin burns.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfur dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfur dioxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sulfur dioxide causes human lung irritation. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfur dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Sulfur dioxide gas is a severe irritant of the eyes, mucous membranes, and skin. Its irritant properties are due to the rapidity with which it forms sulfurous acid on contact with moist membranes. In combination with certain particulate matter and/or oxidants, the effects may be markedly increased. Approximately 90% of all sulfur dioxide inhaled is absorbed in the upper respiratory passages, where most effects occur; however, high concentrations may produce respiratory paralysis and pulmonary edema. Exposure to concentrations of 10 to 50 ppm for 5 to 15 minutes causes irritation of the eyes,

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nose, and throat, rhinorrhea, choking, cough, and, in some instances, reflex bronchoconstriction with increased pulmonary resistance. Some 10 to 20% of the healthy young adult population is estimated to be hypersusceptible to the effects of sulfur dioxide, while the phenomenon of adaptation to irritating concentrations is a recognized occurrence in experienced workers. Workers repeatedly exposed to 10 ppm experienced upper respiratory irritation and some nosebleeds, but the symptoms did not occur at 5 ppm; in another study, initial cough and irritation did occur at 5 ppm and 13 ppm, but subsided after 5 minutes of exposure. In a human experimental study with the subjects breathing through the mouth, brief exposure to 13 ppm caused a 73% increase in pulmonary flow resistance; 5 ppm resulted in a 40% increase; 1 ppm produced no effects. Exposure of the eyes to liquid sulfur dioxide from pressurized containers causes corneal burns and opacification resulting in a loss of vision. The liquid on the skin produces skin burns from the freezing effect of rapid evaporation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 64.1
2. Boiling point (760 mm Hg): −10 C (14 F)
3. Specific gravity (water = 1): 1.46 (liquid)
4. Vapor density (air = 1 at boiling point of sulfur dioxide): 2.26
5. Melting point: −75.5 C (−104 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 10
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with some powdered metals and with alkali metals such as sodium or potassium may cause fires and explosions.
3. Hazardous decomposition products: None.
4. Special precautions: Liquid sulfur dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible
2. Compressed gas cylinders containing sulfur dioxide should be stored in accordance with 29 CFR 1910.101.

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* reports that "Henderson and Haggard gave the odor threshold as 3 to 5 ppm."
2. Eye Irritation Level: Patty states that "20 ppm is the least amount irritating to the eyes."
3. Other Information: Patty states that "sulfur dioxide is an irritant gas: 6 to 12 ppm causes immediate irritation to nose and throat. Three tenths to 1 ppm can be detected by the average individual, probably by taste rather than by odor, and 3 ppm has an easily noticeable odor."
4. Evaluation of Warning Properties: Through odor and taste, sulfur dioxide can be detected at or below the permissible exposure limit. Nose and throat irritation occur within three times the permissible exposure limit. For the purposes of this guideline, therefore, sulfur dioxide is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of gas in a hydrogen peroxide-filled impinger with a subsequent chemical analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sulfur dioxide may be used. An analytical method for sulfur dioxide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid sulfur dioxide or from contact with vessels containing liquid sulfur dioxide.
- Any clothing which becomes wet with liquid sulfur dioxide should be removed immediately and not reworn until the sulfur dioxide has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid sulfur dioxide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid sulfur dioxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sulfur dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Use as bleaching and preservative agent in wood and pulp, sugar and food preparation industries; as a selective antiseptic in food industry and as a fumigating agent in ships	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as solvent in oil refineries; during synthesis in chemical, petroleum, textile, pharmaceutical, tanning, photography, metal, and rubber industries	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as refrigerant in commercial refrigerators	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during extraction, enrichment, and recovery processes in mining and metallurgy industry	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous processes during leather tanning, special glass manufacture, water treatment, textile processing, and chrome waste treatment	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid sulfur dioxide or strong concentrations of sulfur dioxide gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid sulfur dioxide gets on the skin, immediately flush the contaminated skin with water. If liquid sulfur dioxide penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of sulfur dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If sulfur dioxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in liquid form, allow to vaporize.

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RESPIRATORY PROTECTION FOR SULFUR DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
20 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against sulfur dioxide.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
100 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against sulfur dioxide. A gas mask with a chin-style or a front- or back-mounted canister providing protection against sulfur dioxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against sulfur dioxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Sulfuric Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H_2SO_4
- Synonyms: Oil of vitriol
- Appearance and odor: Colorless to dark brown, oily, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfuric acid is 1 milligram of sulfuric acid per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 1 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Sulfuric Acid should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfuric acid can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Sulfuric acid may cause irritation of the eyes, nose, and throat. Breathing in the mist or vapor may cause teeth erosion or the mouth to become sore and also difficulty in breathing. Splashes in the eyes or on the skin will cause severe skin burns.
2. Long-term Exposure: Repeated or prolonged exposure to dilute solutions of sulfuric acid may cause irritation of the skin. Repeated or prolonged exposure to mists or vapors of sulfuric acid may cause erosion of the teeth, chronic irritation of the eyes, or chronic inflammation of the nose, throat, and bronchial tubes.
3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfuric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfuric acid at potentially hazardous levels:
1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, eyes, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sulfuric acid may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfuric acid is reported to cause pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Sulfuric acid mist severely irritates the eyes, respiratory tract, and skin. Concentrated sulfuric acid destroys tissue due to its severe dehydrating action, whereas the dilute form acts as a milder irritant due to acid properties. The LC50 of mist of 1-micron particle size for an 8 hour exposure was 50 mg/m^3 for adult guinea pigs and 18 mg/m^3 for young animals. Continuous exposure of guinea pigs to 2 mg/m^3 for 5 days caused pulmonary edema and thickening of the alveolar walls; exposure of guinea pigs to 2 mg/m^3 for 1 hour caused an increase in

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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pulmonary airway resistance from reflex bronchoconstriction. A worker sprayed in the face with liquid fuming sulfuric acid suffered skin burns of the face and body, as well as pulmonary edema from inhalation. Sequelae were pulmonary fibrosis, residual bronchitis, and pulmonary emphysema; in addition, necrosis of the skin resulted in marked scarring. In human subjects, concentrations of about 5 mg/m^3 were objectionable, usually causing cough, an increase in respiratory rate, and impairment of ventilatory capacity. Workers exposed to concentrations of 12.6 to 35 mg/m^3 had a markedly higher incidence of erosion and discoloration of teeth than was noted in unexposed individuals. Splashed in the eye, the concentrated acid causes extremely severe damage, often leading to blindness, whereas dilute acid produces more transient effects from which recovery may be complete. Repeated exposure of workers to the mist causes chronic conjunctivitis, tracheobronchitis, stomatitis, and dermatitis, as well as dental erosion. While ingestion of the liquid is unlikely in ordinary industrial use, the highly corrosive nature of the substance may be expected to produce serious mucous membrane burns of the mouth and esophagus.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98
2. Boiling point (760 mm Hg): 270 C (518 F)
3. Specific gravity (water = 1): 1.84
4. Vapor density (air = 1 at boiling point of sulfuric acid): 3.4
5. Melting point: 3 C (37 F)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of acid with organic materials (such as chlorates, carbides, fulminates, and picrates) may cause fires and explosions. Contact of acid with metals may form toxic sulfur dioxide fumes and flammable hydrogen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfuric acid fume, sulfur dioxide, and carbon monoxide) may be released when sulfuric acid decomposes.
4. Special precautions: Liquid sulfuric acid will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Sulfuric acid is not combustible by itself, but is highly reactive and capable of igniting finely divided combustible materials on contact. Fires involving small amounts of combustibles may be smothered with dry chemical. Water applied directly to sulfuric acid causes evolution of heat and splattering.

- **Warning properties**

The International Labour Office (ILO) reports that sulfuric acid, in liquid or vapor form, can cause eye irritation, but no quantitative information is given. The NIOSH criteria document for sulfuric acid states that Bushtueva exposed 10 human subjects to different concentrations of sulfuric acid aerosol. At a concentration of 1.1 to 2.4 mg/m^3, 40% of the subjects experienced eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of sulfuric acid on a cellulose membrane filter, followed by extraction with distilled water and isopropyl alcohol, treatment with perchloric acid, and titration with barium perchlorate. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sulfuric acid may be used. An analytical method for sulfuric acid is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid sulfuric acid or solutions containing more than 1% sulfuric acid by weight.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing 1% or less sulfuric acid by weight.
- Where there is any possibility of exposure of an employee's body to liquid sulfuric acid or solutions containingmore than 1% sulfuric acid by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with sulfuric acid should be removed immediately and not reworn until the sulfuric acid is removed from the clothing.
- Clothing contaminated with sulfuric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sulfuric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sulfuric acid, the person performing the operation should be informed of sulfuric acid's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid sulfuric acid or solutions containing sulfuric acid contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid sulfuric acid or solutions containimore than 1% sulfuric acid by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with sulfuric acid should be immediately washed or showered to remove any sulfuric acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sulfuric acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of phosphoric acid and fertilizers	Process enclosure; local exhaust ventilation; personal protective equipment
Use in petroleum refining as an alkylation catalyst for production of high-octane gasoline, production of jet fuels, kerosene, lube and white oils, oil additives, and preparation of cracking catalysts	Process enclosure; local exhaust ventilation; personal protective equipment
Use during manufacture of pigments and dyes, and dyestuff intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of industrial and military explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of alcohols, phenols, and inorganic sulfates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in ore leaching and processing; use in metal cleaning and plating; manufacture of electrogalvanized wire; anodizing of metal; electroplating	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of detergents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in coke-oven gas refining; use in plastics industry for manufacture of rayon, cellophane, cellulose, acetate, caprolactam, and others; use in lead storage batteries as electrolyte	Process enclosure; local exhaust ventilation; personal protective equipment
Use in food processing in manufacture of brewing sugars for beer, manufacture of glucose, refining of mineral and vegetable oils	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use for preparation of insecticides; use in manufacture of natural and synthetic rubber	Process enclosure; local exhaust ventilation; personal protective equipment
Use for gas drying to dry acid and corrosive gases; use in treatment of industrial water for pH control	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of textiles and leather for treatment of wool, pickling leather, as a dye assist, as a solvent for vat dyes, and in fabric finishing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory reagent as a solvent and for chemical analysis; use in chemical synthesis in preparation of acids, intermediates for medicinals, gas, esters, and fatty acids	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid sulfuric acid or solutions containing sulfuric acid get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid sulfuric acid or solutions containing sulfuric acid get on the skin, immediately flush the contaminated skin with water. If liquid sulfuric acid or solutions containing sulfuric acid penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of sulfuric acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid sulfuric acid or solutions containing sulfuric acid have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sulfuric acid. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If sulfuric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled or leaked material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Sulfuric acid should be absorbed in vermiculite, dry sand, earth, or a similar material. It may also be diluted and neutralized.

- Waste disposal method:

Sulfuric acid may be placed in sealed containers or absorbed in vermiculite, dry sand, earth, or a similar material and disposed of in a secured sanitary landfill. It may also be diluted and neutralized.

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RESPIRATORY PROTECTION FOR SULFURIC ACID

Condition	**Minimum Respiratory Protection* Required Above 1 mg/m^3**
Particulate Concentration	
50 mg/m^3 or less	A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter. A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Sulfur Monochloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: S_2Cl_2
- Synonyms: Sulfur chloride; sulfur subchloride
- Appearance and odor: Amber to red fuming, oily liquid with a pungent, nauseating, and irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfur monochloride is 1 part of sulfur monochloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of sulfur monochloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfur monochloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Vapors of sulfur monochloride may cause coughing, and tearing and burning of the eyes which may be delayed in onset. Inhalation of high concentrations of sulfur monochloride may cause severe difficulty in breathing and symptoms of chemical pneumonia. If splashed on the skin, sulfur monochloride liquid may cause irritation, and, if allowed to remain on the skin, a burn. If the liquid is splashed in the eyes, it may produce severe, immediate damage and scarring.

2. Long-term Exposure: Repeated exposure of the skin, eyes, or upper respiratory tract to sulfur monochloride may cause chronic irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfur monochloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfur monochloride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, skin, and eyes should be stressed.

—14" x 17" chest roentgenogram: Sulfur monochloride is a respiratory irritant. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfur monochloride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Sulfur monochloride is a severe irritant of the eyes, mucous membranes, and skin. On contact with water it decomposes to form hydrogen chloride and sulfur dioxide; since this occurs rapidly, it acts primarily as an upper respiratory irritant and does not ordinarily reach the lungs. Exposure of mice to 150 ppm for 1 minute is fatal. In humans, exposure to the vapor causes lacrimation and cough; exposure to high concentrations may cause pulmonary edema. Concentrations of 2 to 9 ppm are reported to be mildly irritating. Splashes of the

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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liquid in the eyes will produce severe immediate damage which may result in permanent scarring. The liquid on the skin will produce irritation and burns if not removed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 135
2. Boiling point (760 mm Hg): 138 C (280 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of sulfur monochloride): 4.66
5. Melting point: −76 C (−105 F)
6. Vapor pressure at 20 C (68 F): 6.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts violently, forming hydrochloric acid
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 300 C (572 F) cause decomposition to toxic chlorine gas and solid sulfur.
2. Incompatibilities: Contact with peroxides, oxides of phosphorus, and some organic matter may cause fires and explosions. Contact with water causes a violent reaction, forming hydrogen chloride gas (or hydrochloric acid), which may corrode metal containers and form flammable hydrogen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, sulfur dioxide, hydrogen sulfide, and carbon monoxide) may be released in a fire involving sulfur monochloride.
4. Special precautions: Sulfur monochloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 118.5 C (245 F) (closed cup)
2. Autoignition temperature: 234 C (453 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No information is available concerning the odor threshold of sulfur monochloride.
2. Eye Irritation Level: According to Grant, "even 2 to 9 ppm in air are said to be mildly irritating to the eyes."
3. Evaluation of Warning Properties: Since sulfur monochloride causes eye irritation within twice the permissible exposure limit, this substance is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for sulfur monochloride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid sulfur monochloride.
- Clothing contaminated with sulfur monochloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sulfur monochloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sulfur monochloride, the person performing the operation should be informed of sulfur monochloride's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid sulfur monochloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with sulfur monochloride should be removed immediately and not reworn until the sulfur monochloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any

possibility of liquid sulfur monochloride contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquid sulfur monochloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with sulfur monochloride should be immediately washed or showered to remove any sulfur monochloride.
- Employees who handle liquid sulfur monochloride should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sulfur monochloride may occur and control methods which may be effective in each case:

Operation	Controls
Use for production of white vulcanized oils used for coating and impregnating textiles; use as natural and synthetic rubber extenders and modifying agents in erasers, and extruded rubber goods	Process enclosure; local exhaust ventilation; personal protective equipment
Use with unsaturated fatty acids in production of additives to extreme pressure lubricants and cutting oils	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a cross-linking catalyst in polymer technology; use in chemical synthesis for production of intermediates for dyes, pharmaceuticals, insecticides, and war gases	Process enclosure; local exhaust ventilation; personal protective equipment
Use for treatment of drying oils for production of varnishes, inks, paints, and cements; use for cold vulcanizing of thin rubber articles; use as a solvent for sulfur and sulfur compounds	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid sulfur monochloride or strong concentrations of sulfur monochloride vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid sulfur monochloride or strong concentrations of sulfur monochloride vapor get on the skin, immediately flush the contaminated skin with water. If liquid sulfur monochloride or strong concentrations of sulfur monochloride vapor penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of sulfur monochloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid sulfur monochloride has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the sulfur monochloride. Do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If sulfur monochloride is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Spray on a thick layer of a (1:1) mixture of dry soda ash and slaked lime. Mix and spray on water slowly, then add large amounts of water. The neutralized solution can then be disposed in a secured sanitary landfill.

- Waste disposal method:

Sulfur monochloride may be disposed of by using (2) above.

REFERENCES

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RESPIRATORY PROTECTION FOR SULFUR MONOCHLORIDE

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
10 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) for hydrogen chloride and sulfur dioxide.
	A gas mask with a chin-style or a front- or back-mounted canister for hydrogen chloride and sulfur dioxide.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen chloride and sulfur dioxide.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Sulfur Pentafluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: S_2F_{10}
- Synonyms: Disulfur decafluoride
- Appearance and odor: Colorless liquid or gas with an odor like sulfur dioxide.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfur pentafluoride is 0.025 part of sulfur pentafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.25 milligram of sulfur pentafluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfur pentafluoride can affect the body if it is inhaled. No data could be found in the literature which specifically reported possible effects of eye or skin contact with the liquid or the effects of ingestion.

- **Effects of overexposure**

1. Short-term Exposure: In animals, inhalation has been reported to cause severe breathing difficulties.

2. Long-term Exposure: Not known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfur pentafluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfur pentafluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system and the cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Sulfur pentafluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfur pentafluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Sulfur pentafluoride vapor is a severe pulmonary irritant. Exposure of rats to 1 ppm for 16 to 18 hours was fatal; 0.5 ppm caused pulmonary edema and hemorrhage; 0.1 ppm caused irritation of the lungs; 0.01 ppm had no discernible effects. Nonfatal exposure of rats for 1 hour to 10 ppm caused pulmonary hemorrhage. In rabbits the LD50 for intravenous injection of a lecithin emulsion of sulfur pentafluoride was 5.8 mg/kg; at autopsy the chief lesion was massive pulmonary edema with frequent hemorrhage, apparently a result of widespread endothelial damage to the cardiovascular system.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 254
  2. Boiling point (760 mm Hg): 29 C (84 F)
  3. Specific gravity (water = 1): 2.08 (at 0 C)
  4. Vapor density (air = 1 at boiling point of sulfur

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pentafluoride): 8.75

5. Melting point: −55 C (−67 F)
6. Vapor pressure at 20 C (68 F): 561 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 400 C (752 F) cause decomposition and development of pressure in containers.
2. Incompatibilities: None
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: According to the International Labour Office (ILO), "no data are available on its effects on the upper respiratory tract and conjunctivae."
3. Evaluation of Warning Properties: Since no quantitative information available relating its warning properties to air concentrations, sulfur pentafluoride is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for sulfur pentafluoride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid sulfur pentafluoride or liquids containing sulfur pentafluoride.
- Clothing contaminated with sulfur pentafluoride should be stored in such a manner that the sulfur pentafluoride is not dispersed until it can be discarded, or until provision is made for the removal of sulfur pentafluoride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sulfur pentafluoride, the person performing the operation should be informed of sulfur pentafluoride's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid sulfur pentafluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with sulfur pentafluoride should be removed immediately and not reworn until the sulfur pentafluoride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid sulfur pentafluoride or liquids containing sulfur pentafluoride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid sulfur pentafluoride or liquids containing sulfur pentafluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.
- Employees should immediately evacuate the area whenever sulfur pentafluoride is accidentally released into the workplace air.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sulfur pentafluoride may occur and control methods which may be effective in each case:

Operation	Controls
Liberation as a by-product during synthesis of sulfur hexafluoride (This compound is considered more toxic than phosgene and is not produced commercially).	Provisions should be made to exit vapors so that they are absorbed by activated alumina and soda lime

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid sulfur pentafluoride or liquids containing sulfur pentafluoride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid sulfur pentafluoride or liquids containing sulfur pentafluoride get on the skin, immediately flush the contaminated skin with water. If liquid sulfur pentafluoride or liquids containing sulfur pentafluoride penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of sulfur pentafluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If liquid sulfur pentafluoride or liquids containing sulfur pentafluoride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sulfur pentafluoride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If sulfur pentafluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of leak.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If liquid, allow liquid to evaporate.

ADDITIONAL INFORMATION

To find additional information on sulfur pentafluoride, look up sulfur pentafluoride in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR SULFUR PENTAFLUORIDE

Condition	**Minimum Respiratory Protection* Required Above 0.025 ppm**
Vapor Concentration	
0.25 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Sulfuryl Fluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: SO_2F_2
- Synonyms: None
- Appearance and odor: Colorless and odorless gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfuryl fluoride is 5 parts of sulfuryl fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 20 milligrams of sulfuryl fluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfuryl fluoride can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Animal experiments have shown that inhalation of sulfuryl fluoride may cause shaking, convulsions, and severe breathing difficulties. Human exposure to a mixture of sulfuryl fluoride and an irritant gas caused nausea, vomiting, crampy abdominal pain, itching, reddening of the eyes, nose, and throat, and minor lung changes. These effects were of short duration.

2. Long-term Exposure: Animal experiments have shown that repeated exposure to sulfuryl fluoride may cause mottled teeth and kidney and lung injury.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfuryl fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfuryl fluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system and the central nervous system should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Sulfuryl fluoride gas is a respiratory irritant and a depressant of the central nervous system. Although there are few details, exposure of animals to an unspecified but high concentration caused signs of narcosis and, in some instances, tremor, convulsions, and pulmonary edema; repeated exposure caused lung and kidney injury. A worker who was exposed to an undetermined concentration of a mixture of sulfuryl fluoride and an undesignated irritant gas for 4 hours developed nausea, vomiting, abdominal pain, and pruritis; examination revealed conjunctivitis, rhinitis, pharyngitis, diffuse rhonchi, and paresthesia of the right leg, all of which rapidly subsided.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.1
2. Boiling point (760 mm Hg): −55.2 C (−67 F)
3. Specific gravity (water = 1): 1.36 (liquid)
4. Vapor density (air = 1 at boiling point of sulfuryl fluoride): 3.5
5. Melting point: −136.7 C (−213 F)
6. Vapor pressure at 20 C (68 F): Greater than 1

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atmosphere

7. Solubility in water, g/100 g water at 20 C (68 F): 0.16

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause cylinders to burst.

2. Incompatibilities: None

3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and hydrogen fluoride) may be released when sulfuryl fluoride decomposes.

4. Special precautions: See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Spector states that sulfuryl fluoride is odorless.

2. Eye Irritation Level: Baskin states that sulfuryl fluoride is severely irritating to the eyes. Other sources do not mention this severe eye irritation, however, and no quantitative information is available concerning the threshold of eye irritation. Gleason states that "chronic exposure . . . . to 100 ppm resulted in no adverse effects on rats, rabbits, guinea pigs, or monkeys."

3. Other Information: Baskin states that sulfuryl fluoride is severely irritating to the mucous membranes of the respiratory tract. No quantitative information is available concerning the threshold of this irritation, however.

4. Evaluation of Warning Properties: Since sulfuryl fluoride is odorless, and since no quantitative information is available relating its irritant effects to air concentrations, this substance is treated as a material with poor warning properties. Taxay states that sulfuryl fluoride has no warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for sulfuryl fluoride is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sulfuryl fluoride may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use as an insecticidal fumigant for control of dry wood termites and other structural pests	Process enclosure; mix with alerting gas

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If strong concentrations of sulfuryl fluoride gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Breathing**

If a person breathes in large amounts of sulfuryl fluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Under-

stand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If sulfuryl fluoride is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty into a mixed solution of caustic soda and slaked lime.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Sulfuryl Fluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Baskin, A. D. (ed.): *Handling Guide for Potentially Hazardous Commodities*, Railway Systems and Management Association, Chicago, 1972.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
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- Taxay, E. P.: "Vikane Inhalation," *Journal of Occupational Medicine*, 8:425-426, 1966.

RESPIRATORY PROTECTION FOR SULFURYL FLUORIDE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Gas Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against sulfuryl fluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 2,4,5-T *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cl_3C_6H_2OCH_2COOH$
- Synonyms: 2,4,5-Trichlorophenoxyacetic acid
- Appearance and odor: Colorless to tan odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2,4,5-T is 10 milligrams of 2,4,5-T per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2,4,5-T can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to 2,4,5-T may cause abdominal pain, nausea, vomiting, diarrhea, and blood in the stool. It may also cause irritation of the skin. Common contaminants of commercial preparations of 2,4,5-T may cause acne and liver damage. Animal experiments have shown that these contaminants may produce damage in unborn rats.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2,4,5-T.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2,4,5-T at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and attention to gastrointestinal complaints should be stressed. The skin should be examined for evidence of chronic disorders.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

2,4,5-T (2,4,5-trichlorophenoxyacetic acid) is of low toxicity. The oral LD50 for dogs is in the range of 100 mg/kg or higher; effects are limited to a slight or moderate stiffness in the hind legs with development of ataxia. Contaminants of commercial preparations of 2,4,5-T have been 2,3,7,8-tetrachlorodibenzo-p-dioxin, a potent animal teratogen, and 2,3,6,7-tetrachlorodibenzo-p-dioxin (TCDD), a potent acnegenic agent which is hepatotoxic in animals; they are present as unwanted side products of synthesis of 2,4,5-T. In a study of 73 workers in a 2,4,5-T manufacturing plant, 13 had moderate to severe acneform dermatitis (chloracne) and 22 had gastrointestinal complaints such as nausea, vomiting, diarrhea, abdominal pain, or blood in the stool; no significant liver dysfunction was found; although no air sample results were reported, the chloracne was thought to be a result of exposure to TCDD. 2,4,5-T dust is a slight irritant of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 255.5
2. Boiling point (760 mm Hg): Decomposes above melting point
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of 2,4,5-T): Not applicable
5. Melting point: 158 C (316 F) (decomposition)

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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6. Vapor pressure at 20 C (68 F): Essentially zero

7. Solubility in water, g/100 g water at 20 C (68 F): 0.03

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 158 C (316 F) may cause sealed metal containers to burst.

2. Incompatibilities: None.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when 2,4,5-T decomposes.

4. Special precautions: None.

- **Flammability**

1. Not combustible

- **Warning properties**

2,4,5-T is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 2,4,5-T is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

- Eating and smoking should not be permitted in areas where 2,4,5-T is handled, processed, or stored.
- Employees who handle 2,4,5-T should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2,4,5-T may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of herbicides and plant hormones	Process enclosure; local exhaust ventilation; personal protective equipment
Application as herbicide, defoliant, and plant hormone	Personal protective equipment
Manufacture of 2,4,5-T	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 2,4,5-T gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 2,4,5-T or liquids containing 2,4,5-T get on the skin, wash the contaminated skin using soap or mild detergent and water. If 2,4,5-T or liquids containing 2,4,5-T soak through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 2,4,5-T, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 2,4,5-T or liquids containing 2,4,5-T have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If 2,4,5-T is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing 2,4,5-T should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

2,4,5-T may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "2,4,5-T (2,4,5-Trichlorophenoxacetic Acid)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
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- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Khera, K. S., and McKinley, W. P.: "Pre- and Post-Natal Studies on 2,4,5-Trichlorophenoxyacetic Acid, 2,4-Dichlorophenoxyacetic Acid and Their Derivatives in Rats," Toxicology and Applied Pharmacology, 22:14-28, 1972.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Poland, A. P., et al.: "A Health Survey of Workers in a 2,4-D and 2,4,5-T Plant," *Archives of Environmental Health*, 22:316-327, 1971.
- Spencer, E. Y.: *Guide to the Chemicals Used in Crop Protection* (6th ed.), Publication 1093, Research Branch Agriculture, Canada, 1973.

* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR 2,4,5-T

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any dust and mist respirator, except single-use.
100 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
500 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Talc (Non-Asbestos Form)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: No specific formula
- Synonyms: Hydrous magnesium silicate; steatite talc; non-fibrous talc; non-asbestiform talc
- Appearance and odor: Odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for talc is 20 million particles of talc per cubic foot of air (mppcf) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for talc (non-asbestos form) from 20 mppcf to 15 mppcf or 2 mg/m^3 respirable dust.

- **Method**

At the time of publication of this guideline, no measurement method for talc had been published by NIOSH.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Talc can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

Repeated inhalation of non-asbestos form of talc dust might cause scarring of the lungs with shortness of breath, chronic cough, and heart failure. The non-asbestos form of talc may cause irritation of the eyes in the same manner as nuisance dusts.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to talc.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to talc at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: The non-asbestos form of talc may have the potential to cause pulmonary fibrosis and cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Talc is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The non-asbestos form of talc, also termed nonfibrous, has been reported to cause talcosis although this is controversial. It has not been proven to cause the effects produced by exposure to fibrous talc: fibrotic pneumoconiosis and an increased incidence of cancer of the lungs and pleura. In a study of 20 workers exposed for 10 to 36 years to talc described as "pure," at levels ranging from 15 to 35 mppcf, no evidence of pneumoconiosis was found. In another study which compared the pulmonary function of workers exposed to either fibrous or nonfibrous talc, it was concluded that while the fibrous form was the more pathogenic type, both talcs produced pulmonary fibrosis; no data were presented to document the types of talc involved. An epidemiologic study of 260 workers with 15 or more

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years of exposure to commercial talc dust containing pure talc, plus tremolite, anthophyllite, carbonate dusts, and a small amount of free silica revealed a fourfold greater than expected proportional mortality from cancer of the lungs and pleura; in addition, a major cause of death was cor pulmonale, a result of the pneumoconiosis; the effects were likely due to the asbestos-form contaminants. The role of nonfibrous talc in these disease states could not be assessed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 295
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.5 – 2.8
  4. Vapor density (air = 1 at boiling point of talc): Not applicable
  5. Melting point: 900 – 1000 C (1652 – 1832 F) (loses water)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Talc is not reported to be a significant eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of talc in an impinger, followed by dust counting utilizing an optical microscope. A detailed analytical method for talc may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set R" (order number PB 262 403).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to talc may occur and control methods which may be effective in each case:

Operation	Controls
Use in cosmetic industry as face powder, body or dusting powder, soap, and toilet preparations; in pharmaceutical industry in tablets, pills, salves, and lotions	General dilution ventilation; dust collecting system; wet grinding; personal protective equipment
Liberation during mining and processing by crushing, drying, milling, and upgrading by flotation	General dilution ventilation; dust collecting system; wet grinding; personal protective equipment
Use as a filler and selective absorbent in paper industry; use in ceramics industry in high quality electronic products as insulation; use as a selective absorbent in rubber and plastics reinforcing; use in cleaning up oil spills	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If the non-asbestos form of talc gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If talc is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Talc may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR TALC (NON-ASBESTOS FORM)

Condition	Minimum Respiratory Protection* Required Above 20 mppcf
Particulate Concentration	
100 mppcf or less	Any dust and mist respirator.
200 mppcf or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
1000 mppcf or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 mppcf or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 mppcf or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Tantalum Metal and Oxide Dusts

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

Metallic tantalum

- Formula: Ta
- Synonyms: None
- Appearance and odor: Gray-black, odorless solid.

Tantalum pentoxide

- Formula: Ta_2O_5
- Synonyms: None
- Appearance: Colorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tantalum is 5 milligrams of tantalum per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tantalum can affect the body if it is inhaled.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tantalum.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to tantalum at potentially hazardous levels.

- **Summary of toxicology**

Tantalum dust has a low order of toxicity but has produced transient inflammatory lesions in the lungs of animals. Intratracheal administration of tantalum oxide to guinea pigs produced transient bronchitis, interstitial pneumonitis, and hyperemia. There were some slight residual sequelae in the form of focal hypertrophic emphysema and organizing pneumonitis around metallic deposits; there was slight epithelial hyperplasia in the bronchi and bronchioles.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Metallic tantalum**

1. Molecular weight: 180.9
2. Boiling point (760 mm Hg): 5425 C (9997 F)
3. Specific gravity (water = 1): 16.6
4. Vapor density (air = 1 at boiling point of tantalum): Not applicable
5. Melting point: 2980 C (5396 F)
6. Vapor pressure at 20 C (68 F): 0 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Tantalum pentoxide**

1. Molecular weight: 441.89
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 8.2
4. Vapor density (air = 1 at boiling point of tantalum pentoxide): Not applicable
5. Melting point: 1800 C (3272 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity—Metallic tantalum**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of tantalum (metallic dust) with strong oxidizers may cause fires and explo-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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sions.

3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability-Metallic tantalum**

1. Flash point: Not applicable
2. Minimum ignition temperature: 300 C (572 F) (layer); 630 C (1166 F) (cloud)
3. Minimum explosion dust concentration: Less than 0.2 g/l
4. Extinguishant: Dry sand, dry dolomite, and dry graphite

- **Warning properties**

Tantalum is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for tantalum is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tantalum metal and oxide dusts may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during refining ores, manufacture of tantalum compounds, metal, and alloys	General dilution ventilation; local exhaust ventilation
Use in fabrication for manufacture of electronic equipment such as electrolytic capacitors used in solid-state circuitry for computers, instrumentation, and consumer items, and high-voltage surge arrestors	General dilution ventilation; local exhaust ventilation
Use in fabrication of metals for manufacture of chemical and metallurgical processing equipment and heat exchanger	General dilution ventilation; local exhaust ventilation
Use in fabrication of refractory non-ferrous alloys for nuclear and aerospace applications; use in manufacture of tantalum carbide for working machinery; use in manufacture of surgical metals, mesh, and clips; use in manufacture of special optical glass; and use in manufacture and repair of glass-lined equipment	General dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of metallic tantalum dust or tantalum oxide dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES— Metallic tantalum and tantalum pentoxide

- Persons not wearing protective equipment should be restricted from areas of spills until cleanup has been completed.
- If potentially hazardous amounts of metallic tantalum or tantalum pentoxide are spilled or released, the following steps should be taken:

1. Remove all ignition sources in the case of a spill or release of metallic tantalum dust.
2. Ventilate area of spill or release.
3. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal method:

Tantalum and tantalum pentoxide may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR TANTALUM

Condition	**Minimum Respiratory Protection*** **Required Above 5 mg/m^3**
Dust or Mist Concentration	
25 mg/m^3 or less	Any dust and mist respirator.
50 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
50 mg/m^3 or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
10,000 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for TEDP

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5)_4P_2S_2O_5$
- Synonyms: Tetraethyl pyrophosphorodithionate; sulfotepp; tetraethyl dithionopyrophosphate; tetraethyl dithiopyrophosphate
- Appearance and odor: Yellow liquid wtih a garlic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for TEDP is 0.2 milligram of TEDP per cubic meter of air (mg/m³) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

TEDP can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of TEDP, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing TEDP, loss of appetite, nausea, vomiting, abdominal cramps, and diarrhea may appear within 2 hours. After skin absorption, sweating and twitching in the area of absorption may occur usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to all the above symptoms, weakness, generalized twitching, and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heartbeat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to levels of TEDP may make a person more susceptible to the effects of this and related chemicals. Repeated exposure to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to TEDP.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to TEDP at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, and attention to the cholinesterase levels in the blood should be stressed.

—Cholinesterase determination: TEDP causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed quarterly or at any

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time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

TEDP (tetraethyl dithionopyrophosphate) is an anticholinesterase agent; absorption may occur from inhalation of the mist, by skin absorption, or ingestion of the liquid. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscles, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms occurs promptly and almost always within 12 hours. After inhalation, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within one week; increased susceptibility to the effects of anticholinesterase agents persists for one to several days after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 322.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.19
4. Vapor density (air = 1 at boiling point of TEDP): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0025
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, phosphoric acid mist, and carbon monoxide) may be released when TEDP decomposes.
4. Special precautions: TEDP will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information available concerning the odor threshold of TEDP.
2. Eye Irritation Level: TEDP is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of TEDP, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for TEDP had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted

are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with TEDP.
- Clothing contaminated with TEDP should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of TEDP from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the TEDP, the person performing the operation should be informed of TEDP's hazardous properties.
- Where there is any possibility of exposure of an employee's body to TEDP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with TEDP should be removed immediately and not reworn until the TEDP is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of TEDP contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to TEDP, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with TEDP should be immediately washed or showered with soap or mild detergent and water to remove any TEDP.
- Eating and smoking should not be permitted in areas where TEDP is handled, processed, or stored.
- Employees who handle TEDP should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to TEDP may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of insecticides	Process enclosure; local exhaust ventilation; personal protective equipment
Application of insecticide by aerosol or fumigation on flowering plants in commercial greenhouses	Personal protective equipment
Manufacture of TEDP	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If TEDP or formulations containing TEDP get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If TEDP or formulations containing TEDP get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If TEDP or formulations containing TEDP penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of TEDP, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When TEDP or formulations containing TEDP have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If TEDP is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

TEDP may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR TEDP

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Particulate or Vapor Concentration	
2 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
35 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 35 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of TEDP; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 35 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Tellurium and Compounds (as Tellurium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all tellurium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Tellurium

- Formula: Te
- Synonyms: Tellurium, metallic
- Appearance and odor: Odorless, grayish-colored solid with a metallic luster.

Hydrogen telluride

- Formula: H_2Te
- Synonyms: Tellurium hydride
- Appearance and odor: Colorless gas with a characteristic odor like arsenic.

Potassium tellurite

- Formula: K_2TeO_3
- Synonyms: None
- Appearance and odor: White, odorless solid.

Sodium tellurate

- Formula: $Na_2H_4TeO_6$
- Synonyms: Sodium tellurate dihydrate
- Appearance and odor: White, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tellurium and compounds (as tellurium) is 0.1 milligram of tellurium and compounds (as tellurium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tellurium and compounds can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed. They may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Tellurium, hydrogen telluride, potassium tellurite, or sodium tellurate causes garlic odor of the breath and sweat, dryness of the mouth, metallic taste, sleepiness, loss of appetite, and nausea. Tellurium dioxide exposure may cause a temporary loss of sweat function.

2. Long-term Exposure: Tellurium hydride is highly toxic. It has produced irritation of the lungs and destruction of red blood cells in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tellurium and compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tellurium and compounds at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from tellurium and compounds exposure.

—Skin disease: Tellurium can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Neurologic disorders: By analogy to effects observed in experimental animals, tellurium may adversely affect the nervous system in man.

—Blood disease: Hydrogen telluride is reported to cause hemolysis in animals. Persons with pre-existing blood disorders may be at increased risk from exposure.

—Chronic respiratory disease: Hydrogen telluride and other gaseous compounds of tellurium are reported to cause pulmonary effects. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of certain compounds of tellurium might cause exacerbation of symptoms.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination. The concentration of tellurium in the urine may be informative when exposures are high. Garlic odor of the breath is a sensitive sign of tellurium exposure.

- **Summary of toxicology**

Fume or dust of tellurium and its compounds causes garlic odor of the breath and malaise in humans. In animals, acute tellurium intoxication results in restlessness, tremor, diminished reflexes, paralysis, convulsions, somnolence, coma, and death. Tellurium compounds are more toxic than the metal. Administration to pregnant rats of 500 to 3000 ppm tellurium in the diet resulted in high incidence of hydrocephalic offspring. Weaning rats fed elemental tellurium at a level of 1% (10,000 ppm) in the diet developed a neuropathy characterized by segmental demyelination; remyelination and functional recovery occurred despite continued administration of tellurium. Iron foundry workers exposed to concentrations between 0.01 to 0.1 mg/m^3 complained of garlic odor of the breath and sweat, dryness of the mouth and metallic taste, somnolence, anorexia, and occasional nausea; urinary concentrations ranged from zero to 0.06 mg/l; somnolence and metallic taste in the mouth did not appear with regularity until the level of tellurium in the urine was at least 0.01 mg/l. Skin lesions in the form of scaly, itching patches and loss of sweat function occurred in workers exposed to tellurium dioxide in an electrolytic lead refinery. Hydrogen telluride is highly toxic and has caused pulmonary irritation and hemolysis of red blood cells in animals; this gas is very unstable, however, and its occurrence as an actual industrial hazard is unlikely.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Tellurium**

1. Molecular weight: 127.6
2. Boiling point (760 mm Hg): 1390 C (2534 F)
3. Specific gravity (water = 1): 6.24
4. Vapor density (air = 1 at boiling point of tellurium): Not applicable
5. Melting point: 450 C (842 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Hydrogen telluride**

1. Molecular weight: 129.6
2. Boiling point (760 mm Hg): −2 C (28 F)
3. Specific gravity (water = 1): 2.6 (liquid)
4. Vapor density (air = 1 at boiling point of hydrogen telluride): 4.5
5. Melting point: −50 C (−58 F)
6. Vapor pressure at 20 C (68 F): 1600 mm Hg approximately
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Potassium tellurite**

1. Molecular weight: 253.8
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of potassium tellurite): Not applicable
5. Melting point: 450 C (842 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Sodium tellurate**

1. Molecular weight: 273.6
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of sodium tellurate): Not applicable
5. Melting point: 170 C (338 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None. (Hydrogen telluride is unstable, but is rarely worked with as such).
2. Incompatibilities: Contact of tellurium metal or hydrogen telluride with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: a) Tellurium: 340 C (644 F) (layer); 550 C (1022 F) (cloud); b) Hydrogen telluride: Data not available; c) Potassium tellurite and d) sodium tellurate: Not applicable
3. Flammable limits in air, % by volume: Tellurium, potassium tellurite, and sodium tellurate: Not applicable; Hydrogen telluride: Data not available
4. Extinguishant: Tellurium: Water; Hydrogen telluride: Rarely handled as such; Potassium tellurite and

sodium tellurate: Not applicable

- **Warning properties**

Tellurium is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by treatment with nitric and perchloric acids, solution in nitric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for tellurium and compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).
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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with hydrogen telluride or from contact with vessels containing hydrogen telluride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with potassium tellurite, sodium tellurate, or liquids containing these compounds.
- If employees' clothing may have become contaminated with potassium tellurite, sodium tellurate, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with potassium tellurite or sodium tellurate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Any clothing which becomes wet with liquid hydrogen telluride should be removed immediately and not reworn until the hydrogen telluride has evaporated.
- Non-impervious clothing which becomes contaminated with potassium tellurite should be removed promptly and not reworn until the potassium tellurite is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid hydrogen telluride may contact the eyes.

SANITATION

- Skin that becomes contaminated with potassium tellurite should be promptly washed or showered to remove any contaminant.
- Eating and smoking should not be permitted in areas where potassium tellurite, sodium tellurate, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle potassium tellurite, sodium tellurate, or liquids containing these compounds should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tellurium and compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during recovery, purification, and packaging	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during manufacture of alloys with copper, steel, lead, tin, silver, magnesium, nickel, and phosphorus; during use in manufacture of cast iron; liberation during refining of various minerals	Process enclosure or local exhaust ventilation; personal protective equipment
Liberation during use in manufacture of natural and synthetic rubber and plastics	Process enclosure or local exhaust ventilation; personal protective equipment
Use in manufacture of tellurium compounds used as insecticides, germicides, fungicides, and photographic print toners	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use in ceramic colorants and glass manufacture; during manufacture of thermoelectric devices for cooling boxes, solar energy converters, and small control apparatus; during manufacture of electronic devices such as batteries, solar cells, and semiconductors, and during manufacture of tellurium compounds	Process enclosure or local exhaust ventilation; personal protective equipment
Liberation during refining of various minerals; during use as a catalyst for acrylic monomer production	Process enclosure or local exhaust ventilation; personal protective equipment
Use in manufacture of tellurium compounds used as insecticides, germicides, fungicides, and photographic print toners	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If tellurium and compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If tellurium and compounds get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tellurium and compounds penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of tellurium and compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tellurium and compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tellurium and compounds are spilled, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing tellurium and compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.
3. For hydrogen telluride, stop flow of gas.

- Waste disposal method:

Tellurium and compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Tellurium," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR TELLURIUM AND COMPOUNDS (AS TELLURIUM)

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m³**
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Tellurium Hexafluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: TeF_6
- Synonyms: None
- Appearance and odor: Colorless gas with a repulsive odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tellurium hexafluoride is 0.02 part of tellurium hexafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of tellurium hexafluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tellurium hexafluoride can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Tellurium hexafluoride may cause a garlic odor to the breath, headaches, and difficulty in breathing. Tellurium exposure experience with animals indicates that delayed severe breathing difficulties might occur.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tellurium hexafluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tellurium hexafluoride at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from tellurium hexafluoride exposure.

—Chronic respiratory disease: Tellurium hexafluoride causes respiratory irritation. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of tellurium hexafluoride might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Tellurium hexafluoride gas is a severe respiratory irritant. Animals exposed to 1 ppm for 4 hours developed pulmonary edema; 5 ppm for 4 hours was fatal. Human experience has indicated that exposure to tellurium hexafluoride causes headache and dyspnea. No systemic effects have been reported from industrial exposure, but relatively few studies are available.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 241.6
2. Boiling point (760 mm Hg): −38.4 C (−38 F) (sublimes)
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of tellurium hexafluoride): 8.3
5. Melting point: −37.8 C (−36 F) (triple-point)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts slowly
8. Evaporation rate (butyl acetate = 1): Not perti-

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- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride) may be released when tellurium hexafluoride decomposes.
  4. Special precautions: See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.
- **Flammability**
  1. Not combustible
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of tellurium hexafluoride. The *Documentation of TLV's*, however, notes that this gas has an unpleasant odor.
  2. Eye Irritation Level: Tellurium hexafluoride is not known to be an eye irritant.
  3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, this compound is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of tellurium hexafluoride using an adsorption tube, followed by desorption with sodium hydroxide and atomic absorption spectrophotometric analysis. An analytical method for tellurium hexafluoride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tellurium hexafluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use in scientific studies on physical and chemical properties such as magnetic spin, force constants spectra, electron diffraction, crystal structure, and corrosive action	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of tellurium hexafluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If tellurium hexafluoride is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Tellurium Hexafluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Tellurium," *Hygienic Guide Series*, Detroit, Michigan, 1964.
- Cerwenka, E. A., Jr., and Cooper, W. C.: "Toxicology of Selenium and Tellurium and Their Compounds," *Archives of Environmental Health*, 3:189-200, 1961.
- Cooper, W. C.: *Tellurium*, Van Nostrand Reinhold, New York, 1971.

RESPIRATORY PROTECTION FOR TELLURIUM HEXAFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.02 ppm
Gas Concentration	
0.2 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against tellurium hexafluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for TEPP

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5)_4P_2O_7$
- Synonyms: Tetraethyl pyrophosphate, commercial 40%; ethyl pyrophosphate; bladan; nifost; vapotone; tetron; killax; mortopal
- Appearance and odor: Colorless to amber liquid with a faint fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for TEPP is 0.05 milligram of TEPP per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

TEPP can affect the body if it is inhaled or if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of TEPP, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing TEPP, loss of appetite, nausea, vomiting, abdominal cramps, and diarrhea may appear within 2 hours. After skin absorption, sweating and twitching in the area of absorption may occur usually within 15 minutes to 4 hours. With severe intoxiciation by all routes, in addition to the above symptoms, weakness, generalized twitching and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heartbeat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to TEPP may make a person more susceptible to the effects of this and related chemicals. Repeated exposure to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to TEPP.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to TEPP at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system, and attention to the cholinesterase levels in the blood should be stressed.

—Cholinesterase determination: TEPP causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed quarterly or at any

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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time overexposure is suspected or signs or symptoms of toxicity occur.

- **Summary of toxicology**

TEPP (tetraethyl pyrophosphate) is an anticholinesterase agent; absorption may occur from inhalation of the mist, by skin absorption, or by ingestion of the liquid. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscle, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms occurs promptly and almost always within 12 hours. After inhalation, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures, and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within one week; increased susceptibility to the effects of anticholinesterase agents persists for one to several days after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects. Mild intoxication was reported in 15 people exposed to a dust of 1% TEPP under unusual conditions of static air; the predominant symptom was shortness of breath which occurred after breathing the dust-laden air for 30 minutes; symptoms rapidly abated after exposure was terminated.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 290.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of TEPP): Not applicable
5. Melting point: Gradually sets to glass below 0 C (32 F)
6. Vapor pressure at 140 C (284 F): 1 mm
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 150 C (300 F) cause decomposition with formation of flammable ethylene gas.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid mist and carbon monoxide) may be released when TEPP decomposes.
4. Special precautions: TEPP will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of TEPP.
2. Eye Irritation Level: TEPP is not known to produce a local, irritant effect upon the eye. According to Grant, however, when absorbed by the eye, TEPP can cause visual disturbances.
3. Evaluation of Warning Properties: No quantitative information is available relating warning properties to air concentrations of TEPP. TEPP, therefore, is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for TEPP is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with TEPP.
- Clothing contaminated with TEPP should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of TEPP from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the TEPP, the person performing the operation should be informed of TEPP's hazardous properties.
- Where there is any possibility of exposure of an employee's body to TEPP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with TEPP should be removed immediately and not reworn until the TEPP is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of TEPP contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to TEPP, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with TEPP should be immediately washed or showered to remove any TEPP.
- Eating and smoking should not be permitted in areas where TEPP is handled, processed, or stored.
- Employees who handle TEPP should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to TEPP may occur and control methods which may be effective in each case:

Operation	Controls
Application as a contact insecticide on agricultural and ornamental crops, including use in greenhouses	Personal protective equipment
Formulation of insecticides	General dilution ventilation; personal protective equipment
Manufacture of TEPP	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If TEPP or formulations containing TEPP get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If TEPP or formulations containing TEPP get on the skin, immediately wash the contaminated skin with water. If TEPP or formulations containing TEPP penetrate through the clothing, remove the clothing immediately and wash the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of TEPP, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When TEPP or formulations containing TEPP have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If TEPP is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

TEPP may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "TEPP (Tetraethyl Pyrophosphate)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Stolman, A. (ed.): *Progress in Chemical Toxicology*, Academic Press, New York, 1965-1969.

RESPIRATORY PROTECTION FOR TEPP

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m^3
Particulate or Vapor Concentration	
0.5 mg/m^3 or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2.5 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m^3 or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 10 mg/m^3** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of TEPP; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Terphenyls

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{18}H_{14}$
- Synonyms: ortho-Terphenyl; meta-terphenyl; para-terphenyl; mixed terphenyls; diphenylbenzenes; triphenyls
- Appearance: Colorless or light yellow solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for terphenyls is a ceiling of 1 part of terphenyls per million parts of air (ppm). This may also be expressed as 9 milligrams of terphenyls per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for terphenyls a Threshold Limit Value of 0.5 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Terphenyls can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

Exposure to terphenyls may cause eye, skin, and respiratory irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to terphenyls.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to terphenyls at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from terphenyls exposure.

—Skin disease: The hot vapors of the terphenyls have a primary irritant effect on the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Persons with acute or chronic respiratory diseases may be more susceptible to the effects of terphenyls, since transient changes in the mitochondria of alveolar cells have been demonstrated in the lungs of animals following such exposure.

—Liver disease: Persons with liver disease may be more susceptible to the effects of inhalation of terphenyls, since transient changes in hepatic cells have been demonstrated in the liver of animals following such exposure.

—Kidney disease: Although terphenyls are not recognized as renal toxins, the importance of this organ in the excretion of metabolites formed from absorbed terphenyls justifies special consideration in those with possible impairment of renal function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Experimental animals show conjunctival irritation from direct contact with terphenyls. Clinical studies of an exposed group of employees showed no ill effects from prolonged exposure to concentrations ranging from 0.1 to 0.9 mg/m^3. Animals exposed to concentrations of three to five times these levels had slight cellular changes in the lungs and liver, as demonstrated by electron microscopy. Absorbed terphenyls are slowly metabolized and excreted in the urine as phenolic compounds and as glucuronides.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Molecular weight: 230
2. Boiling point (760 mm Hg): 333 to 381 C (630 to 718 F)
3. Specific gravity (water = 1): 1.1 to 1.2
4. Vapor density (air = 1 at boiling point of terphenyls): Not applicable
5. Melting point: 56 to 213 C (133 to 415 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving terphenyls.
4. Special precautions: None

- **Flammability**

1. Flash point: 163 to 207 C (325 to 405 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide or dry chemical

- **Warning properties**

The *Documentation of TLV's* states that "the available toxicologic data indicate that terphenyls may produce eye, skin, and respiratory irritation; they may also cause sensitization, but this has not been shown in man. Workers exposed to dust and vapor experienced marked irritation at concentrations in air above 10 mg/m^3. On this basis, a threshold limit value of 1ppm (about 9.4 mg/m^3) as a ceiling value is recommended to prevent irritation of the eye and respiratory tract."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of terphenyls. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of terphenyls on a filter, followed by leaching with carbon disulfide, and gas chromatographic analysis. An analytical method for terphenyls is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten terphenyls.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid terphenyls or liquids containing terphenyls.
- If employees' clothing may have become contaminated with solid terphenyls, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with terphenyls should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of terphenyls from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the terphenyls, the person performing the operation should be informed of terphenyls's hazardous properties.
- Where there is any possibility of exposure of an employee's body to molten terphenyls, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with terphenyls should be removed promptly and not reworn until the terphenyls are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of molten terphenyls contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

terphenyls or solutions containing terphenyls may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to molten terphenyls, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with terphenyls should be promptly washed or showered with soap or mild detergent and water to remove any terphenyls.
- Employees who handle solid terphenyls or solutions containing terphenyls should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to terphenyls may occur and control methods which may be effective in each case:

Operation	Controls
Use during formulation of waxes, polishes, and resin body paints	Local exhaust ventilation; personal protective equipment
Liberation during application of resin body paints, solvents, waxes, and polishes	Personal protective equipment
Liberation during maintenance operations or following leaks in heat-transfer systems; during release of high-temperature lubricants; during distillation and other processing operations	Personal protective equipment
Liberation during manufacture of plastic scintillators; during process of flaking or crushing to produce solid terphenyls following distillation	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If terphenyls get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If terphenyls dust or solutions containing terphenyls get on the skin, promptly wash or shower to remove any terphenyls from the skin. If molten terphenyls get on the skin, immediately wash or shower the contaminated skin to remove any terphenyls from the skin. If molten terphenyls soak through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of terphenyls, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If terphenyls have been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If terphenyls are spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, use a procedure similar to that for small quantities.

- Waste disposal methods:

Terphenyls may be disposed of:

1. By making packages of terphenyls in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving terphenyls in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Terphenyls," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd

ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR TERPHENYLS

Condition	**Minimum Respiratory Protection* Required Above 9 mg/m^3**
Particulate Concentration	
450 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3500 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3500 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Terphenyls

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{18}H_{14}$
- Synonyms: ortho-Terphenyl; meta-terphenyl; para-terphenyl; mixed terphenyls; diphenylbenzenes; triphenyls
- Appearance: Colorless or light yellow solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for terphenyls is a ceiling of 1 part of terphenyls per million parts of air (ppm). This may also be expressed as 9 milligrams of terphenyls per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for terphenyls a Threshold Limit Value of 0.5 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Terphenyls can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

Exposure to terphenyls may cause eye, skin, and respiratory irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to terphenyls.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to terphenyls at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from terphenyls exposure.

—Skin disease: The hot vapors of the terphenyls have a primary irritant effect on the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Persons with acute or chronic respiratory diseases may be more susceptible to the effects of terphenyls, since transient changes in the mitochondria of alveolar cells have been demonstrated in the lungs of animals following such exposure.

—Liver disease: Persons with liver disease may be more susceptible to the effects of inhalation of terphenyls, since transient changes in hepatic cells have been demonstrated in the liver of animals following such exposure.

—Kidney disease: Although terphenyls are not recognized as renal toxins, the importance of this organ in the excretion of metabolites formed from absorbed terphenyls justifies special consideration in those with possible impairment of renal function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Experimental animals show conjunctival irritation from direct contact with terphenyls. Clinical studies of an exposed group of employees showed no ill effects from prolonged exposure to concentrations ranging from 0.1 to 0.9 mg/m^3. Animals exposed to concentrations of three to five times these levels had slight cellular changes in the lungs and liver, as demonstrated by electron microscopy. Absorbed terphenyls are slowly metabolized and excreted in the urine as phenolic compounds and as glucuronides.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Molecular weight: 230
2. Boiling point (760 mm Hg): 333 to 381 C (630 to 718 F)
3. Specific gravity (water = 1): 1.1 to 1.2
4. Vapor density (air = 1 at boiling point of terphenyls): Not applicable
5. Melting point: 56 to 213 C (133 to 415 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving terphenyls.
4. Special precautions: None

- **Flammability**

1. Flash point: 163 to 207 C (325 to 405 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide or dry chemical

- **Warning properties**

The *Documentation of TLV's* states that "the available toxicologic data indicate that terphenyls may produce eye, skin, and respiratory irritation; they may also cause sensitization, but this has not been shown in man. Workers exposed to dust and vapor experienced marked irritation at concentrations in air above 10 mg/m^3. On this basis, a threshold limit value of 1ppm (about 9.4 mg/m^3) as a ceiling value is recommended to prevent irritation of the eye and respiratory tract."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of terphenyls. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of terphenyls on a filter, followed by leaching with carbon disulfide, and gas chromatographic analysis. An analytical method for terphenyls is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten terphenyls.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid terphenyls or liquids containing terphenyls.
- If employees' clothing may have become contaminated with solid terphenyls, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with terphenyls should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of terphenyls from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the terphenyls, the person performing the operation should be informed of terphenyls's hazardous properties.
- Where there is any possibility of exposure of an employee's body to molten terphenyls, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with terphenyls should be removed promptly and not reworn until the terphenyls are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of molten terphenyls contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

terphenyls or solutions containing terphenyls may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to molten terphenyls, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with terphenyls should be promptly washed or showered with soap or mild detergent and water to remove any terphenyls.
- Employees who handle solid terphenyls or solutions containing terphenyls should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to terphenyls may occur and control methods which may be effective in each case:

Operation	Controls
Use during formulation of waxes, polishes, and resin body paints	Local exhaust ventilation; personal protective equipment
Liberation during application of resin body paints, solvents, waxes, and polishes	Personal protective equipment
Liberation during maintenance operations or following leaks in heat-transfer systems; during release of high-temperature lubricants; during distillation and other processing operations	Personal protective equipment
Liberation during manufacture of plastic scintillators; during process of flaking or crushing to produce solid terphenyls following distillation	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If terphenyls get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If terphenyls dust or solutions containing terphenyls get on the skin, promptly wash or shower to remove any terphenyls from the skin. If molten terphenyls get on the skin, immediately wash or shower the contaminated skin to remove any terphenyls from the skin. If molten terphenyls soak through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of terphenyls, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If terphenyls have been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If terphenyls are spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, use a procedure similar to that for small quantities.

- Waste disposal methods:

Terphenyls may be disposed of:

1. By making packages of terphenyls in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving terphenyls in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Terphenyls," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd

ed., 2nd printing), Cincinnati, 1974.

- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Cornish, H. H., et al.: "Toxicity and Metabolism of Ortho-, Meta-, and Para-Terphenyls," *American Industrial Hygiene Association Journal*, 23:372-378, 1962.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Weeks, J. L., and Lentle, B. C.: "Health Considerations in the Use of Organic Reactor Coolants," *Journal of Occupational Medicine*, 12:246-252, 1970.

RESPIRATORY PROTECTION FOR TERPHENYLS

Condition	**Minimum Respiratory Protection* Required Above 9 mg/m³**
Particulate Concentration	
450 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3500 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Terphenyls

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{18}H_{14}$
- Synonyms: ortho-Terphenyl; meta-terphenyl; para-terphenyl; mixed terphenyls; diphenylbenzenes; triphenyls
- Appearance: Colorless or light yellow solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for terphenyls is a ceiling of 1 part of terphenyls per million parts of air (ppm). This may also be expressed as 9 milligrams of terphenyls per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for terphenyls a Threshold Limit Value of 0.5 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Terphenyls can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

Exposure to terphenyls may cause eye, skin, and respiratory irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to terphenyls.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to terphenyls at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from terphenyls exposure.

—Skin disease: The hot vapors of the terphenyls have a primary irritant effect on the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Persons with acute or chronic respiratory diseases may be more susceptible to the effects of terphenyls, since transient changes in the mitochondria of alveolar cells have been demonstrated in the lungs of animals following such exposure.

—Liver disease: Persons with liver disease may be more susceptible to the effects of inhalation of terphenyls, since transient changes in hepatic cells have been demonstrated in the liver of animals following such exposure.

—Kidney disease: Although terphenyls are not recognized as renal toxins, the importance of this organ in the excretion of metabolites formed from absorbed terphenyls justifies special consideration in those with possible impairment of renal function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Experimental animals show conjunctival irritation from direct contact with terphenyls. Clinical studies of an exposed group of employees showed no ill effects from prolonged exposure to concentrations ranging from 0.1 to 0.9 mg/m^3. Animals exposed to concentrations of three to five times these levels had slight cellular changes in the lungs and liver, as demonstrated by electron microscopy. Absorbed terphenyls are slowly metabolized and excreted in the urine as phenolic compounds and as glucuronides.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Molecular weight: 230
2. Boiling point (760 mm Hg): 333 to 381 C (630 to 718 F)
3. Specific gravity (water = 1): 1.1 to 1.2
4. Vapor density (air = 1 at boiling point of terphenyls): Not applicable
5. Melting point: 56 to 213 C (133 to 415 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving terphenyls.
4. Special precautions: None

- **Flammability**

1. Flash point: 163 to 207 C (325 to 405 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide or dry chemical

- **Warning properties**

The *Documentation of TLV's* states that "the available toxicologic data indicate that terphenyls may produce eye, skin, and respiratory irritation; they may also cause sensitization, but this has not been shown in man. Workers exposed to dust and vapor experienced marked irritation at concentrations in air above 10 mg/m^3. On this basis, a threshold limit value of 1ppm (about 9.4 mg/m^3) as a ceiling value is recommended to prevent irritation of the eye and respiratory tract."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of terphenyls. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of terphenyls on a filter, followed by leaching with carbon disulfide, and gas chromatographic analysis. An analytical method for terphenyls is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten terphenyls.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid terphenyls or liquids containing terphenyls.
- If employees' clothing may have become contaminated with solid terphenyls, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with terphenyls should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of terphenyls from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the terphenyls, the person performing the operation should be informed of terphenyls's hazardous properties.
- Where there is any possibility of exposure of an employee's body to molten terphenyls, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with terphenyls should be removed promptly and not reworn until the terphenyls are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of molten terphenyls contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

terphenyls or solutions containing terphenyls may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to molten terphenyls, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with terphenyls should be promptly washed or showered with soap or mild detergent and water to remove any terphenyls.
- Employees who handle solid terphenyls or solutions containing terphenyls should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to terphenyls may occur and control methods which may be effective in each case:

Operation	Controls
Use during formulation of waxes, polishes, and resin body paints	Local exhaust ventilation; personal protective equipment
Liberation during application of resin body paints, solvents, waxes, and polishes	Personal protective equipment
Liberation during maintenance operations or following leaks in heat-transfer systems; during release of high-temperature lubricants; during distillation and other processing operations	Personal protective equipment
Liberation during manufacture of plastic scintillators; during process of flaking or crushing to produce solid terphenyls following distillation	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If terphenyls get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If terphenyls dust or solutions containing terphenyls get on the skin, promptly wash or shower to remove any terphenyls from the skin. If molten terphenyls get on the skin, immediately wash or shower the contaminated skin to remove any terphenyls from the skin. If molten terphenyls soak through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of terphenyls, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If terphenyls have been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If terphenyls are spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, use a procedure similar to that for small quantities.

- Waste disposal methods:

Terphenyls may be disposed of:

1. By making packages of terphenyls in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving terphenyls in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Terphenyls," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd

ed., 2nd printing), Cincinnati, 1974.

- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Cornish, H. H., et al.: "Toxicity and Metabolism of Ortho-, Meta-, and Para-Terphenyls," *American Industrial Hygiene Association Journal*, 23:372-378, 1962.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Weeks, J. L., and Lentle, B. C.: "Health Considerations in the Use of Organic Reactor Coolants," *Journal of Occupational Medicine*, 12:246-252, 1970.

RESPIRATORY PROTECTION FOR TERPHENYLS

Condition	**Minimum Respiratory Protection* Required Above 9 mg/m^3**
Particulate Concentration	
450 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3500 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3500 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,1,1,2-Tetrachloro-2,2-Difluoroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CCl_3\text{-}CClF_2$
- Synonyms: Halocarbon 112a; refrigerant 112a; 2,2-difluoro-1,1,1,2-tetrachloroethane
- Appearance and odor: Colorless liquid or solid with a slight ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,1,2-tetrachloro-2,2-difluoroethane is 500 parts of 1,1,1,2-tetrachloro-2,2-difluoroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4170 milligrams of 1,1,1,2-tetrachloro-2,2-difluoroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,1,2-Tetrachloro-2,2-difluoroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: 1,1,1,2-Tetrachloro-2,2-difluoroethane might cause irritation of the skin and eyes. It might also cause drowsiness and difficulty in breathing.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,1,2-tetrachloro-2,2-difluoroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1,1,2-tetrachloro-2,2-difluoroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1,1,2-tetrachloro-2,2-difluoroethane exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,1,1,2-tetrachloro-2,2-difluoroethane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,1,1,2-Tetrachloro-2,2-difluoroethane vapor is a narcotic. Rats exposed to 10,000 ppm for 1-½ to 2 hours showed signs of intoxication, and concentrations of 20,000 to 30,000 ppm were fatal. Rats succumbing to 15,000 ppm for 4 hours evidenced pulmonary congestion and edema with some hemorrhage. Application in alcohol to the skin of rabbits produced severe irritation, while no irritation was reported when applied with dimethylphthalate. There are no reports of systemic effects in workers from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 203.8
2. Boiling point (760 mm Hg): 92 C (197 F)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of 1,1,1,2-tetrachloro-2,2-difluoroethane): 7
5. Melting point: 40.6 C (105 F)
6. Vapor pressure at 20 C (68 F): 40 mm Hg (approximately)

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility in water, g/100 g water at 20 C (68 F): 0.012

8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Reacts with chemically active metals such as sodium, potassium, and beryllium, or with powdered magnesium, aluminum, and zinc.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, hydrogen fluoride, and carbon monoxide) may be released when 1,1,1,2-tetrachloro-2,2-difluoroethane decomposes.
4. Special precautions: 1,1,1,2-Tetrachloro-2,2-difluoroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

No quantitative data are available relating warning properties to air concentrations of of this compound. Therefore, for the purposes of this guideline, it is treated as a material with poor warning properties.

1,1,1,2-Tetrachloro-2,2-difluoroethane is not a known eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,1,2-tetrachloro-2,2-difluoroethane may be used. An analytical method for 1,1,1,2-tetrachloro-2,2-difluoroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid or solid 1,1,1,2-tetrachloro-2,2-difluoroethane.
- Non-impervious clothing which becomes contaminated with liquid or solid 1,1,1,2-tetrachloro-2,2-difluoroethane should be removed promptly and not reworn until the 1,1,1,2-tetrachloro-2,2-difluoroethane is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid 1,1,1,2-tetrachloro-2,2-difluoroethane may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid or solid 1,1,1,2-tetrachloro-2,2-difluoroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1,1,2-tetrachloro-2,2-difluoroethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,1,2-tetrachloro-2,2-difluoroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in dry cleaning industry for wool, cotton, dacron, and leather materials in combination with other solvents as azeotropic mixture; use in electric or electronic industries for cleaning rosin fluxes from circuit boards, and cleaning solvent for complex electronic parts and magnetic tapes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer and plastics industry as blowing or foaming agent for cellular and microporous materials	Local exhaust ventilation
Use as solvent extractant for separation and purification of biological material; use as a dye solvent to give brighter colors, and to detect surface cracks or defects in metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as corrosion inhibitors in brake fluid, surface coatings on electrical equipment, heat control of reactions, and propellants	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,1,1,2-tetrachloro-2,2-difluoroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1,1,2-tetrachloro-2,2-difluoroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,1,2-tetrachloro-2,2-difluoroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1,1,2-tetrachloro-2,2-difluoroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1,1,2-tetrachloro-2,2-difluoroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1,1,2-tetrachloro-2,2-difluoroethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the liquid form, collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.
3. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation.

- Waste disposal methods:

1,1,1,2-Tetrachloro-2,2-difluoroethane may be disposed of:

1. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material
2. If in the solid form, by disposing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "1,1,1,2-Tetrachloro-2,2-Difluoroethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Clayton, J. W.: "Toxicity Studies on 1,1,2,2-Tetrachloro-1,2-Difluoroethane and 1,1,1,2-Tetrachloro-2,2-Difluoroethane," *American Industrial Hygiene Association Journal*, 27:332-340, 1966.

way, Cincinnati, Ohio 45226.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE

Condition	**Minimum Respiratory Protection* Required Above 500 ppm**
Vapor Concentration	
5000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
15,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 15,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,1,2,2-Tetrachloro-1,2-Difluoroethane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CCl_2F\text{-}CCl_2F$
- Synonyms: Refrigerant 112; halocarbon 112
- Appearance and odor: Colorless liquid or solid with a slight ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2,2-tetrachloro-1,2-difluoroethane is 500 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4170 milligrams of 1,1,2,2-tetrachloro-1,2-difluoroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2,2-Tetrachloro-1,2-difluoroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: 1,1,2,2-Tetrachloro-1,2-difluoroethane might cause irritation of the skin and eyes. It might also cause drowsiness and difficult breathing.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2,2-tetrachloro-1,2-difluoroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1,2,2-tetrachloro-1,2-difluoroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1,2,2-tetrachloro-1,2-difluoroethane exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,1,2,2-tetrachloro-1,2-difluoroethane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,1,2,2-Tetrachloro-1,2-difluoroethane vapor is a narcotic. Rats exposed to 10,000 ppm for 1-½ to 2 hours showed signs of intoxication; concentrations of 20,000 to 30,000 ppm for the same period were fatal and caused pulmonary hemmorhages. In rats repeatedly exposed for 6 hours to 1,000 ppm, there were no clinical signs of toxicity; some showed slight changes in liver cells, and a few female rats had a decreased leukocyte count. The liquid applied to the intact skin of guinea pigs produced mild irritation in 24 hours. Instilled in the eyes of rabbits, it produced mild conjunctival irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 203.8
2. Boiling point (760 mm Hg): 92.8 C (199 F)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of 1,1,2,2-tetrachloro-1,2-difluoroethane): 7
5. Melting point: 26 C (79 F)
6. Vapor pressure at 20 C (68 F): 40 mm Hg

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7. Solubility in water, g/100 g water at 20 C (68 F): 0.012

8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Reacts with chemically active metals such as sodium, potassium, and beryllium, or with powdered aluminum, zinc, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, hydrogen fluoride, and carbon monoxide) may be released when 1,1,2,2-tetrachloro-1,2-difluoroethane decomposes.
4. Special precautions: 1,1,2,2-Tetrachloro-1,2-difluoroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

No quantitative data are available relating warning properties of 1,1,2,2-tetrachloro-1,2-difluoroethane to its air concentrations. Therefore, this compound is treated as a material with poor warning properties. Deichmann and Gerarde report that 1,1,2,2-tetrachloro-1,2-difluoroethane is mildly irritating to rabbit eyes, but the levels at which irritation occurs are not given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,2,2-tetrachloro-1,2-difluoroethane may be used. An analytical method for 1,1,2,2-tetrachloro-1,2-difluoroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).
(order number PB 265 028).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid or solid 1,1,2,2-tetrachloro-1,2-difluoroethane.
- Non-impervious clothing which becomes wet with liquid 1,1,2,2-tetrachloro-1,2-difluoroethane or contaminated with solid 1,1,2,2-tetrachloro-1,2-difluoroethane should be removed promptly and not reworn until the 1,1,2,2-tetrachloro-1,2-difluoroethane is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid 1,1,2,2-tetrachloro-1,2-difluoroethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 1,1,2,2-tetrachloro-1,2-difluoroethane or contaminated with solid 1,1,2,2-tetrachloro-1,2-difluoroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1,2,2-tetrachloro-1,2-difluoroethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2,2-tetrachloro-1,2-difluoroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in dry cleaning industry for wool, cotton, dacron, and leather materials in combination with other solvents as azeotropic mixture; use in electric or electronic industries for cleaning rosin fluxes from circuit boards, and cleaning solvent for complex electronic parts and magnetic tapes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer and plastics industry as blowing or foaming agent for cellular and microporous materials	Local exhaust ventilation
Use as solvent extractant for separation and purification of biological material; use as a dye solvent to give brighter colors, and to detect surface cracks or defects in metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as corrosion inhibitors in brake fluid, surface coatings on electrical equipment, heat control of reactions, and propellants	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,1,2,2-tetrachloro-1,2-difluoroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1,2,2-tetrachloro-1,2-difluoroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2,2-tetrachloro-1,2-difluoroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1,2,2-tetrachloro-1,2-difluoroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1,2,2-tetrachloro-1,2-difluoroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water.) Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1,2,2-tetrachloro-1,2-difluoroethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the liquid form, collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.
3. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

- Waste disposal methods:

1,1,2,2-Tetrachloro-1,2-difluoroethane may be disposed of:

1. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. If in the solid form, by disposing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "1,1,2,2-Tetrachloro-1,2-Difluoroethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Clayton, J. W., et al.: "Toxicity Studies on 1,1,2,2-

Tetrachloro-1,2-Difluoroethane and 1,1,1,2-Tetrachloro-2,2-Difluoroethane," *American Industrial Hygiene Association Journal*, 27:332-340, 1960.

- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

* SPECIAL NOTE

1,1,2,2-Tetrachloro-1,2-difluoroethane appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE

Condition	**Minimum Respiratory Protection* Required Above 500 ppm**
Vapor Concentration	
5000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
15,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 15,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,1,2,2-Tetrachloroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CHCl_2CHCl_2$
- Synonyms: Symmetrical-tetrachloroethane; acetylene tetrachloride; sym-tetrachlorethane
- Appearance and odor: Colorless or pale yellow liquid with a sickly sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2,2-tetrachloroethane is 5 parts of 1,1,2,2-tetrachloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of 1,1,2,2-tetrachloroethane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm (6.87 mg/m³) averaged over a 10-hour work shift. The NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2,2-Tetrachloroethane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Breathing in high concentrations of 1,1,2,2-tetrachloroethane may cause irritation of the eyes and nose, nausea, vomiting, and drowsiness. Liver and kidney damage may occur. If the exposure was severe, within a few hours a deep dusky coloration of the skin may appear, followed by unconsciousness and death. If the exposed worker is removed immediately, he may recover completely but should be placed under observation in case late symptoms appear. If the vapor or liquid of 1,1,2,2-tetrachloroethane gets into the eyes, it may cause watering and burning. It may cause serious eye damage unless immediate medical care is obtained.

2. Long-term Exposure: Prolonged or repeated exposure to 1,1,2,2-tetrachloroethane, either by breathing or by absorbing it through the skin, may cause fatigue, loss of appetite, tremors, weight loss, constipation, heart damage, blood changes, kidney damage, abdominal distress or pain, vomiting, dizziness, tenderness, liver damage with such symptoms as pain over the liver, dark urine, and yellow jaundice. Reproductive abnormalities have been noted in studies of animals following exposure to high levels of 1,1,2,2-tetrachloroethane. Prolonged or repeated skin contact with 1,1,2,2-tetrachloroethane may also cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2,2-tetrachloroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1,2,2-tetrachloroethane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver, kidneys, and central nervous system should be stressed.

—Liver function tests: 1,1,2,2-Tetrachloroethane causes liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

1,1,2,2-Tetrachloroethane is highly toxic to the liver and is a central nervous system depressant. Rats exposed to 500 ppm for 4 hours survived, but 1,000 ppm was fatal. Reports of industrial experience indicate that cases of mild intoxication have presented symptoms of gastrointestinal irritation (nausea, vomiting, abdominal pain, anorexia) and central nervous system effects (dizziness, headache, irritability, nervousness, insomnia); more severe exposure resulted in liver involvement (enlarged and tender liver, jaundice, bilirubinuria), nephritis (albuminuria and casts); and tremors of hands and eyelids. In cases of severe industrial intoxication, there was hepatic necrosis with jaundice, sometimes progressing to cirrhosis; individuals who died during the acute stage also showed cerebral edema and pulmonary edema with hemorrhage, as well as liver and kidney injury. One study reported that human subjects exposed to 335 ppm for 10 minutes or 186 ppm for 30 minutes noted a disagreeable odor; there were some upper respiratory irritation and central nervous system effects. Among a group of workers in India exposed to 20-65 ppm there was nausea, vomiting, and abdominal pain and a high incidence of tremor of the hands. Prolonged skin exposure may be expected to produce dermatitis due to defatting action. Eye damage has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 167.8
2. Boiling point (760 mm Hg): 146 C (295 F)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of 1,1,2,2-tetrachloroethane): 5.8
5. Melting point: −42.5 C (−44.5 F)
6. Vapor pressure at 20 C (68 F): 8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.29
8. Evaporation rate (butyl acetate = 1): 0.65

- **Reactivity**

1. Conditions contributing to instability: Heat; unusual exposure to light in the presence of air may form small amounts of phosgene.
2. Incompatibilities: Reacts with chemically active metals or with strong caustics. In the presence of steam, contact with hot iron, aluminum, and zinc may cause formation of toxic vapors.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, chlorinated solvents, and carbon monoxide) may be released when 1,1,2,2-tetrachloroethane decomposes.
4. Special precautions: Liquid 1,1,2,2-tetrachloroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Patty states that the odor of 1,1,2,2-tetrachloroethane is detectable at 5 ppm (3 ppm, according to Lehmann). Since the odor threshold is at (or below) the permissible exposure limit, this compound is treated as a material with good warning properties.

Grant indicates that this compound is not an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,2,2-tetrachloroethane may be used. An analytical method for 1,1,2,2-tetrachloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

PB 265 028).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid 1,1,2,2-tetrachloroethane.
- Clothing contaminated with liquid 1,1,2,2-tetrachloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1,2,2-tetrachloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1,2,2-tetrachloroethane, the person performing the operation should be informed of 1,1,2,2-tetrachloroethane's hazardous properties.
- Where exposure of an employee's body to liquid 1,1,2,2-tetrachloroethane may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid 1,1,2,2-tetrachloroethane should be removed immediately and not reworn until the 1,1,2,2-tetrachloroethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid 1,1,2,2-tetrachloroethane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid 1,1,2,2-tetrachloroethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid 1,1,2,2-tetrachloroethane should be immediately washed or showered with soap or mild detergent and water to remove any 1,1,2,2-tetrachloroethane.
- Eating and smoking should not be permitted in areas where liquid 1,1,2,2-tetrachloroethane is handled, processed, or stored.
- Employees who handle liquid 1,1,2,2-tetrachloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2,2-tetrachloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical intermediate in manufacture of tetrachloroethylene and trichloroethylene; use in cleaning and extraction processes; use in chlorination of phthalic anhydride; use in manufacture of cyanogen chloride, polymers, and tetrachloro-alkylphenol	Local exhaust ventilation; general dilution ventilation
Use as a fumigant in greenhouses	Personal protective equipment
Use in manufacture of lacquers and varnishes, paint and varnish removers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use and preparation of insecticides and weed killers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cleaning and degreasing of metals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent in preparation of adhesives	Local exhaust ventilation
Use during addition to aliphatic alcohols and acetates to improve solvency for nitrocellulose and cellulose acetate as in photographic film	Local exhaust ventilation
Use in application of adhesives	General dilution ventilation; personal protective equipment
Use in refining of waxes and resins	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,1,2,2-tetrachloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1,2,2-tetrachloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2,2-tetrachloroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1,2,2-tetrachloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1,2,2-tetrachloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1,2,2-tetrachloroethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

1,1,2,2-Tetrachloroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on 1,1,2,2-tetrachloroethane, look up 1,1,2,2-tetrachloroethane in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane (December 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR 1,1,2,2-TETRACHLOROETHANE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
150 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 150 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Tetrachloroethylene*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CCl_2 = CCl_2$
- Synonyms: Perchloroethylene; perchlorethylene; tetrachlorethylene; perk
- Appearance and odor: Colorless liquid with an odor like chloroform or ether.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetrachloroethylene is 100 parts of tetrachloroethylene per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and a maximum acceptable peak of 300 ppm for 5 minutes in any three-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 50 ppm (339 mg/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 100 ppm (678 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Tetrachloroethylene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetrachloroethylene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Tetrachloroethylene may cause headache, nausea, drowsiness, dizziness, incoordination, and unconsciousness. It may also cause irritation of the eyes, nose, and throat and flushing of the face and neck. In addition, it might cause liver damage with such findings as yellow jaundice and dark urine. The liver damage may become evident several weeks after the exposure.

2. Long-term Exposure: Prolonged or repeated overexposure to liquid tetrachloroethylene may cause irritation of the skin. It might also cause damage to the liver and kidneys.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetrachloroethylene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetrachloroethylene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and the cardiovascular and neurological systems should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Tetrachloroethylene may cause liver damage. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Tetrachloroethylene vapor is a narcotic. Rats did not survive when exposed for longer than 12-18 minutes to 12,000 ppm; when exposed repeatedly to 470 ppm they showed liver and kidney injury. Cardiac arrhythmias

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attributed to sensitization of the myocardium to epinephrine have been observed with certain other chlorinated hydrocarbons, but exposure of dogs to concentrations of 5000 and 10,000 ppm tetrachloroethylene did not produce this phenomenon. Four human subjects were unable to tolerate 5000 ppm in a chamber for 6 minutes. They experienced vertigo, nausea, and mental confusion during the 10 minutes following cessation of exposure. In an industrial exposure to an average concentration of 275 ppm for 3 hours, followed by 1100 ppm for 30 minutes, a worker lost consciousness; there was apparent clinical recovery 1 hour after exposure but the monitored concentration of tetrachloroethylene in the patient's expired air diminished slowly over a 2-week period. Long-term industrial exposures have been reported to cause various neuropathies, such as numbness, trembling, neuritis, and defects of memory. During the second and third post-exposure weeks, the results of liver function tests became abnormal, suggesting that acute exposure had had a significant effect upon the liver. Other instances of liver injury following industrial exposure have been reported. Other effects on humans of inhalation of various concentrations are as follows: 2000 ppm, mild narcosis within 5 minutes; 600 ppm, sensation of numbness around the mouth, dizziness, and some incoordination after 10 minutes. In human experiments, 7-hour exposures at 100 ppm resulted in mild irritation of the eyes, nose, and throat; flushing of the face and neck; headache; somnolence; and slurred speech. Exposure of the skin to the liquid for 40 minutes resulted in a progressively severe burning sensation beginning within 5 to 10 minutes; the result was marked erythema, which subsided after 1 to 2 hours. The liquid sprayed into rabbits' eyes produced immediate pain and blepharospasm; patches of epithelium were lost, but the eyes recovered completely within 2 days.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 165.85
2. Boiling point (760 mm Hg): 121.2 C (250 F)
3. Specific gravity (water = 1): 1.62
4. Vapor density (air = 1 at boiling point of tetrachloroethylene): 5.83
5. Melting point: −22.4 C (−8 F)
6. Vapor pressure at 20 C (68 F): 14 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): 2.8

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Tetrachloroethylene reacts with strong oxidizers and chemically active metals such as barium, lithium, and beryllium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released when tetrachloroethylene decomposes.
4. Special precautions: Liquid tetrachloroethylene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Both May and Stern state that 50 ppm is the odor threshold for tetrachloroethylene.
2. Eye Irritation Level: Grant reports that "exposure to high concentrations of (tetrachloroethylene) vapor causes mild sensation of irritation to the eyes, but serious injury is not likely." The exact concentrations producing irritation are not mentioned by Grant.

Spector, however, reports that after a 20- to 30-minute exposure to 206 to 235 ppm, eye irritation occurs in humans.

Patty reports "very slight irritation of the eyes" among humans at 106 ppm.

3. Other Information: Spector reports that a 10-minute exposure to 513 to 690 ppm produces nose and throat irritation.
4. Evaluation of Warning Properties: Since the odor threshold of tetrachloroethylene is below the permissible exposure limit, and since eye irritation occurs at a concentration only twice the permissible exposure limit, its warning properties are considered to be adequate.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of tetrachloroethylene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of tetrachloroethylene. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure tetrachloroethylene may be used. An analytical method for tetrachloroethylene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid tetrachloroethylene.
- Non-impervious clothing which becomes contaminated with liquid tetrachloroethylene should be removed promptly and not reworn until the tetrachloroethylene is removed from the clothing.
- Clothing wet with liquid tetrachloroethylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetrachloroethylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetrachloroethylene, the person performing the operation should be informed of tetrachloroethylene's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid tetrachloroethylene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid tetrachloroethylene should be promptly washed or showered with soap or mild detergent and water to remove any tetrachloroethylene.
- Employees who handle liquid tetrachloroethylene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetrachloroethylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as dry cleaning solvent; as degreasing and metal cleaning agent; in vapor degreasing of metal parts	Local exhaust ventilation; general dilution; personal protective equipment
Use as chemical intermediate in production of fluorocarbons, pesticides, and trichloroacetic acid	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as scouring, sizing, desizing, solvent and greaser remover in processing and finishing of textiles	Local exhaust ventilation; general dilution; personal protective equipment
Use as general industrial solvent in rubber, textile, printing, soap, and paint remover industries	Local exhaust ventilation; general dilution; personal protective equipment
Use as extraction agent for vegetable and mineral oils and in pharmaceutical industry; as vermifuge; as laundry treatment for presoaking and as drying medium in metal and wood industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If tetrachloroethylene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If tetrachloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tetrachloroethylene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of tetrachloroethylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tetrachloroethylene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tetrachloroethylene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Tetrachloroethylene may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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* SPECIAL NOTE

Tetrachloroethylene appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR TETRACHLOROETHYLENE

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4-µm median cut point CAS: None RTECS: None

METHOD: 0600, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 January 1998

OSHA :	5 mg/m^3
NIOSH:	no REL
ACGIH:	3 mg/m^3

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates non-ciliated portions of respiratory system

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER:	CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell [HD] cyclone, or Aluminum cyclone + tared 5-µm PVC membrane)
FLOW RATE:	nylon cyclone: 1.7 L/min HD cyclone: 2.2 L/min Al cyclone: 2.5 L/min
VOL-MIN:	20 L @ 5 mg/m^3
-MAX:	400 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.5 to 10 mg/m^3 (lab and field)
BIAS:	dependent on dust size distribution [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	dependent on size distribution [1,2]
ACCURACY:	dependent on size distribution [1]

MEASUREMENT

TECHNIQUE:	GRAVIMETRIC (FILTER WEIGHT)
ANALYTE:	mass of respirable dust fraction
BALANCE:	0.001 mg sensitivity; use same balance before and after sample collection
CALIBRATION:	National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights
RANGE:	0.1 to 2 mg per sample
ESTIMATED LOD:	0.03 mg per sample
PRECISION:	<10 µg with 0.001 mg sensitivity balance; <70 µg with 0.01 mg sensitivity balance [3]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. In addition to inert dusts [4], the method has been recommended for respirable coal dust. The method is biased in light of the recently adopted international definition of respirable dust, e.g., ≈ +7% bias for non-diesel, coal mine dust [5].

INTERFERENCES: Larger than respirable particles (over 10 µm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in samples are known to be caused by inverting the cyclone assembly. Heavy dust loadings, fibers, and water-saturated dusts also interfere with the cyclone's size-selective properties. The use of conductive samplers is recommended to minimize particle charge effects.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
   a. Filter: 5.0-µm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported by a cassette filter holder (preferably conductive).
   b. Cyclone: 10-mm nylon(Mine Safety Appliance Co., Instrument Division, P. O. Box 427, Pittsburgh, PA 15230), Higgins-Dewell(BGI Inc., 58 Guinan St., Waltham, MA 02154)[7], aluminum cyclone (SKC Inc., 863 Valley View Road, Eighty Four, PA 15330), or equivalent.
2. Personal sampling pump, 1.7 L/min ± 5% for nylon cyclone, 2.2 L/min ± 5% for HD cyclone, or 2.5 L/min ± 5% for the Al cyclone with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of 0.001 mg.
4. Weights, NIST Class S-1.1, or ASTM Class 1.
5. Static neutralizer, e.g., Po-210; replace nine months after the production date.
6. Forceps (preferably nylon).
7. Environmental chamber or room for balance, e.g., 20 °C ± 1 °C and 50% ± 5% RH.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
2. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps (nylon forceps if further analyses will be done).
   c. Pass the filter over an anti-static radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
3. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette.
4. Remove the cyclone's grit cap before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone may be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
5. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

6. Calibrate each personal sampling pump to the appropriate flow rate with a representative sampler in line.
   NOTE 1: Because of their inlet designs, nylon and aluminum cyclones are calibrated within a large vessel with inlet and outlet ports. The inlet is connected to a calibrator (e.g., a bubble meter). The cyclone outlet is connected to the outlet port within the vessel, and the vessel outlet is attached to the pump. See APPENDIX for alternate calibration procedure. (The calibrator can be connected directly to the HD cyclone.)
   NOTE 2: Even if the flowrate shifts by a known amount between calibration and use, the nominal flowrates are used for concentration calculation because of a self-correction feature of the cyclones.
7. Sample 45 min to 8 h. Do not exceed 2 mg dust loading on the filter. Take 2 to 4 replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).
   NOTE : Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in an environmentally controlled area or chamber.

CALIBRATION AND QUALITY CONTROL:

9. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
10. The set of replicate field samples should be exposed to the same dust environment, either in a laboratory dust chamber [8] or in the field [9]. The quality control samples must be taken with the same equipment, procedures, and personnel used in the routine field samples. Calculate precision from these replicates and record relative standard deviation (S_r) on control charts. Take corrective action when the precision is out of control [8].

MEASUREMENT:

11. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloading, leakage, wet, torn, etc.).

CALCULATIONS:

12. Calculate the concentration of respirable particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \cdot 10^3,\ mg/m^3$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B_1 = mean tare weight of blank filters (mg).
B_2 = mean post-sampling weight of blank filters (mg)
V = volume as sampled at the nominal flowrate (i.e., 1.7 L/min or 2.2 L/min)

EVALUATION OF METHOD:

1. Bias: In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust convention. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international convention for respirable dust, the cyclones' penetration curves, and the size distribution of the ambient dust. Based on measured penetration curves for non-pulsating flow [1], the bias in this method is shown in Figure 1.

   For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for some workplace aerosols. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

   Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [12] showed that cyclone samples with pulsating flow can have negative bias as large as –0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias magnitude is less than 0.02 for most dust size distributions encountered in the workplace.

   Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [13] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem. Use of conductive samplers and filter cassettes(Omega Specialty Instrument Co., 4 Kidder Road, Chelmsford, MA 01824) is recommended.

2. Precision: The figure 0.068 mg quoted above for the precision is based on a study [3] of weighing procedures employed in the past by the Mine Safety and Health Administration (MSHA) in which filters are pre-weighed by the filter manufacturer and post-weighed by MSHA using balances readable to 0.010 mg. MSHA [14] has recently completed a study using a 0.001 mg balance for the post-weighing, indicating imprecision equal to 0.006 mg.

   Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [8] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [15] of repeat filter weighings, although the actual attainable precision may depend strongly on the specific environment to which the filters are exposed between the two weighings.

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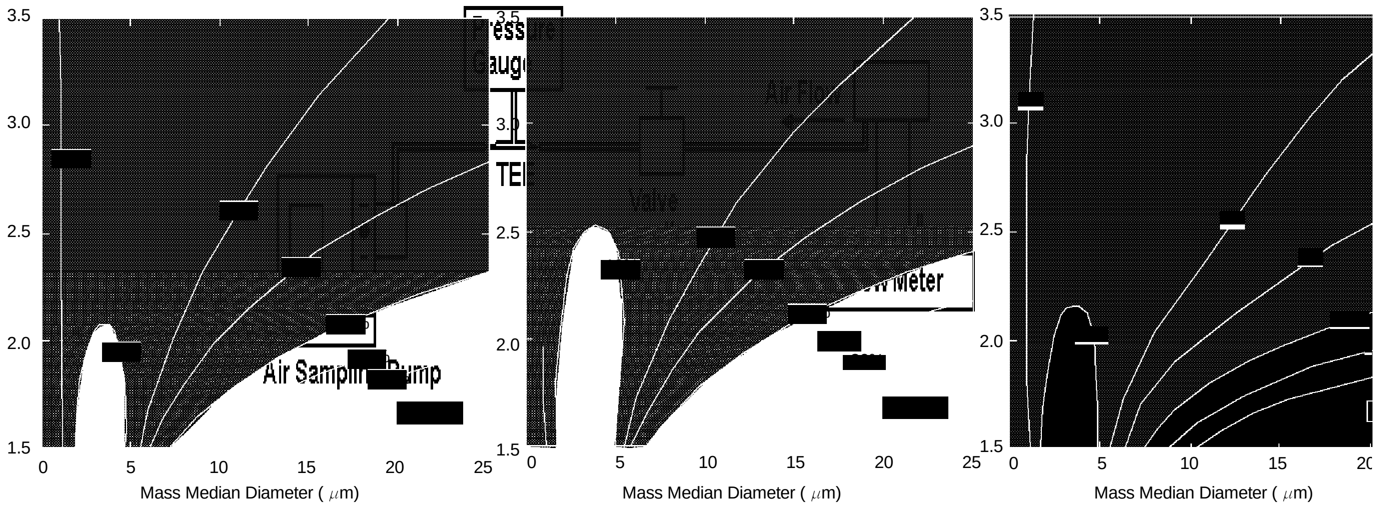
METHOD REVISED BY: David L. Bartley, Ph.D., NIOSH/DPSE/ARDB and Ray Feldman, OSHA.



10-mm nylon cyclone at 1.7 L/min

Higgins-Dewell cyclone at 2.2 L/min

Aluminum cyclone at 2.5 L/m

Figure 1. Bias of three cyclone types relative to the international respirable dust samp convention.

APPENDIX: Jarless Method for Calibration of Cyclone Assemblies

This procedure may be used in the field to calibrate an air sampling pump and a cyclone assembly without using the one-liter “calibration jar”.

(1) Connect the pump to a pressure gauge or water manometer and a light load (adjustable valve or 5-µm filter) equal to 2" to 5" H_2O with a “TEE” connector and flexible tubing. Connect other end of valve to an electronic bubble meter or standard bubble tube with flexible tubing (See Fig. 2.1).
NOTE: A light load can be a 5-µm filter and/or an adjustable valve. A heavy load can be several 0.8-µm filters and/or adjustable valve.

(2) Adjust the pump to 1.7 L/min, as indicated on the bubble meter/tube, under the light load conditions (2" to 5" H_2O) as indicated on the pressure gauge or manometer.

(3) Increase the load until the pressure gauge or water manometer indicates between 25" and 35" H_2O. Check the flow rate of the pump again. The flow rate should remain at 1.7 L/min ± 5%.

(4) Replace the pressure gauge or water manometer and the electronic bubble meter or standard bubble tube with the cyclone having a clean filter installed (Fig. 2.2). If the loading caused by the cyclone assembly is between 2" and 5" H_2O, the calibration is complete and the pump and cyclone are ready for sampling.

Figure 2.1 Block Diagram of Pump/Load/Flow Meter Set-up.

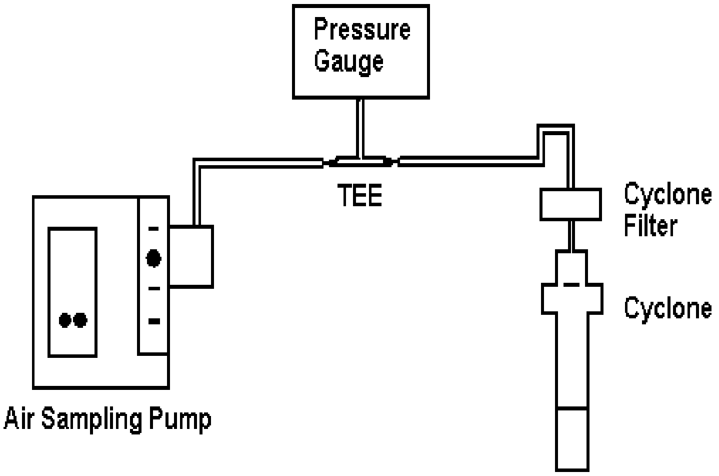


Figure 2.2. Block Diagram with Cyclone as the Test Load.

Occupational Health Guideline for Tetraethyl Lead

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Pb(C_2H_5)_4$
- Synonyms: TEL; lead tetraethyl; motor fuel antiknock compound
- Appearance and odor: Colorless liquid (or dyed red, orange, or blue) with a slight musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetraethyl lead is 0.075 milligrams of tetraethyl lead per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended that the permissible exposure limit be changed to 0.1 mg/m³. The American Conference of Governmental Industrial Hygienists has recommended for tetraethyl lead a Threshold Limit Value of 0.1 mg/m³ with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetraethyl lead can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may readily enter the body through the skin.

- **Effects of overexposure**

The absorption by humans of a sufficient quantity of tetraethyl lead either briefly at a high rate or for prolonged periods at a lower rate may cause intoxication. The onset of symptoms may be delayed for up to eight days after termination of exposure. The milder toxic effects are difficulty in sleeping, tiredness, wild dreams, anxiety, trembling, spasms, slow heart beat, low body temperature, paleness, nausea and loss of appetite. More severe intoxication causes episodes of disorientation, hallucinations, grimacing, and intense activity which requires that the person be restrained. These episodes may convert into manic or violent convulsive seizures which may end in unconsciousness or death. Tetraethyl lead may cause irritation of the eyes. Fetal damage may occur from exposure of the mother to tetraethyl lead, by analogy to methyl mercury.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetraethyl lead.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetraethyl lead at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of mental disorders or hypotension would be expected to be at increased risk from exposure. Examination of the central nervous system and the cardiovascular system should be stressed.

—Urinalysis: Normal kidney function is considered necessary for biologic monitoring. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The concentration of lead should be determined. Urine specimens with a specific gravity less than 1.020 should be discarded and another sampled obtained.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that the determination of lead in the urine should be repeated quarterly.

- **Summary of toxicology**

Tetraethyl lead vapor affects the nervous system and

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causes mental aberrations including psychosis, mania, and convulsions. Of 41 female Swiss mice which survived for 36 weeks after a single subcutaneous injection of 0.6 mg, 5 developed malignant lymphomas during the next 15 weeks; the significance of these data cannot be evaluated, because this tumor occurs spontaneously with a variable incidence in the mouse strain used. The absorption by humans of a sufficient quantity of tetraethyl lead, either briefly at a high rate (100 mg/m^3 for 1 hour) or for prolonged periods at a lower rate, causes acute intoxication; chronic intoxication has not been observed. The onset of symptoms may be delayed for up to 8 days after termination of exposure. The milder manifestations of intoxication are insomnia, lassitude, lurid dreams, dream-like waking states of anxiety, tremor, hyperreflexia, spasmodic muscular contractions, bradycardia, hypotension, hypothermia, pallor, nausea, and anorexia. More severe intoxication causes recurrent or nearly continuous episodes of disorientation, hallucinations, facial contortions, and intense hyperactivity which requires that the individual be restrained. Such episodes may convert abruptly into manic or violent convulsive seizures which may terminate in coma and death. During intoxication there is a striking elevation of the rate of excretion of lead in the urine but only a negligible or slight elevation of the concentration of lead in the blood. In severe intoxication, the urine lead is rarely less than 350 ug/l of urine, while the blood lead is rarely more than 50 ug/100 g of blood. There is also a total absence of morphological or chemical abnormalities in the erythrocytes, in sharp contrast to intoxication caused by inorganic lead. In a mortality study of 592 workers, the mean exposure time was 17.9 years, and urinary lead levels during this period did not exceed 180 ug/l; the incidence of death in this group and in a control group of employees was less than that expected in the general population, and there were no peculiarities in the specific causes of death in either group. In a similar study of a different cohort of these exposed workers, there were no significant health differences when compared with a control group. Although tetraethyl lead may be irritating to the eyes, this effect is considered insignificant when compared with the effects on the central nervous system.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 323.4
2. Boiling point (760 mm Hg): Decomposes above 100 C (212 F)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of tetraethyl lead): 8.6
5. Melting point: −138 to −130 C (−216 to −202 F)
6. Vapor pressure at 20 C (68 F): 0.2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 100 C (212 F) cause decomposition and development of pressure that may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers, such as sulfuryl chloride or potassium permangonate, may cause fires and explosions.
3. Hazardous decomposition products: Toxic airborne substances (such as lead fumes and carbon monoxide) may be released in a fire involving tetraethyl lead.
4. Special precautions: Tetraethyl lead will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 93 C (200 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of tetraethyl lead. The AIHA *Hygienic Guide* states that this substance "has a characteristic sweetish odor, but the intensity of the odor is not adequate to warn of hazardous concentrations."
2. Eye Irritation Level: Grant states that "concerning local effects on the eye from direct contact, there was recorded by Leake in 1926 a strange account of a contamination of the eyes from a splash of gasoline containing tetraethyl lead, after which the patient was said to have been unable to see for three-fourths of an hour. In the course of two months the patient was reported improved and was found to have no corneal or ophthalmoscopic abnormality, but was thought to have slight mydriasis, photophobia, and contraction of the visual field. Very likely the initial difficulty in seeing was due to smarting sensation in the eyes and blepharospasm. The evidence of later eye abnormality in this case seems quite indefinite and questionable.

   "I have tested high-test gasoline containing tetraethyl lead by dropping on rabbit eyes, and have found it to cause immediate pain and blepharospasm lasting several minutes. When the application was repeated ten times in the course of five minutes under local anesthesia, it produced conjunctival hyperemia and moderate flocculent discharge, but no damage to cornea or conjunctiva."
3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of tetraethyl lead, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for tetraethyl lead is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon).
- Clothing contaminated with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon) should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetraethyl lead from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetraethyl lead, the person performing the operation should be informed of tetraethyl lead's hazardous properties.
- If employees' clothing has had any possibility of being contaminated with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon), employees should change into uncontaminated clothing before leaving the work premises.
- Non-impervious clothing which becomes contaminated with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon) should be removed immediately and not reworn until the tetraethyl lead is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid tetraethyl lead may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetraethyl lead may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture in preparation of antiknock agents for fuels	Process enclsoure; local exhaust ventilation; personal protective equipment
Liberation during formulation at petroleum refinery for use as an antiknock agent	Local exhaust ventilation; total enclosure; personal protective devices

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid tetraethyl lead or strong concentrations of tetraethyl lead vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid tetraethyl lead or strong concentrations of tetraethyl lead vapors get on the skin, immediately rinse the contaminated skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. If liquid tetraethyl lead or strong concentrations of tetraethyl lead vapors penetrate through the clothing, remove the clothing immediately and first rinse the skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of tetraethyl lead, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tetraethyl lead has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tetraethyl lead is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Tetraethyl lead may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR TETRAETHYL LEAD

Condition	Minimum Respiratory Protection* Required Above 0.075 mg/m³
Vapor Concentration	
0.75 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3.75 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of tetraethyl lead; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 40 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Tetrahydrofuran

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_4H_8O
- Synonyms: Diethylene oxide; tetramethylene oxide; THF
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetrahydrofuran is 200 parts of tetrahydrofuran per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 590 milligrams of tetrahydrofuran per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetrahydrofuran can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to tetrahydrofuran may cause irritation of the eyes and nose, nausea, dizziness, and headache.

2. Long-term Exposure: Prolonged or repeated exposure to tetrahydrofuran may cause drying of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetrahydrofuran.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetrahydrofuran at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from tetrahydrofuran exposure.

—Skin disease: Tetrahydrofuran can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although tetrahydrofuran is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although tetrahydrofuran is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of tetrahydrofuran might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Tetrahydrofuran is an anesthetic agent and a mild upper respiratory tract irritant. Exposure of animals to vapor above 3000 ppm for 8 hours daily for 20 days produced irritation of the upper respiratory tract. Some injury to the liver and kidneys was observed, which was possibly due to impurities, since other studies have not confirmed this finding. Concentrations above 25,000 ppm produced anesthesia, with a small margin of safety between anesthesia and death. Severe headaches were

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noted among technicians performing this experiment. Daily 6-hour exposures of dogs for 3 to 4 weeks at 200 ppm produced only a slight change in pulse pressure, but no other signs were noted, even when continued for a total of 9 weeks followed by an additional 3 weeks' exposure at nearly 400 ppm. This substance was irritating to the skin of rabbits when applied in aqueous solutions exceeding 20% concentration, although it has not been observed to be a significant skin irritant or sensitizer in industrial practice. No chronic systemic effects have been reported in humans, although nausea, dizziness, and headaches are said to occur with overexposure and are readily reversible in fresh air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72
2. Boiling point (760 mm Hg): 66 C (151 F)
3. Specific gravity (water = 1): 0.9
4. Vapor density (air = 1 at boiling point of tetrahydrofuran): 2.5
5. Melting point: −108 C (−163 F)
6. Vapor pressure at 20 C (68 F): 145 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 14.5

- **Reactivity**

1. Conditions contributing to instability: Heat and sunlight
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving tetrahydrofuran.
4. Special precautions: Tetrahydrofuran will attack some forms of plastics, rubber, and coatings. Storage in the presence of air and light causes the formation of explosive peroxides that remain dissolved in tetrahydrofuran. Containers may explode when their caps or stoppers are removed.

- **Flammability**

1. Flash point: −14.5 C (6 F) (closed cup)
2. Autoignition temperature: 321 C (610 F)
3. Flammable limits in air, % by volume: Lower: 2; Upper: 11.8
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May and Summer both report an odor threshold for tetrahydrofuran of 30 ppm.
2. Eye Irritation Level: Sax reports that tetrahydrofuran is an eye irritant, and Stecher, Browning, and the ILO indicate that it is a mucous membrane irritant, but the concentrations which produce irritation are not given. The *Handbook of Organic Industrial Solvents* reports that tetrahydrofuran "may cause irritation to mucuous membranes at concentrations higher than the threshold limit," but no quantitative information is available concerning the threshold of eye irritation.
3. Other Information: "The TLV of 200 ppm is recommended to protect against irritative effects and has a wide margin of safety for narcotic and systemic effects," according to the *Documentation of TLV's.*
4. Evaluation of Warning Properties: Since the odor threshold of tetrahydrofuran is well below the permissible exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of tetrahydrofuran vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure tetrahydrofuran may be used. An analytical method for tetrahydrofuran is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid tetrahydrofuran.
- Clothing wet with liquid tetrahydrofuran should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetrahydrofuran from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetrahydrofuran, the person performing the operation should be informed of tetrahydrofuran's hazardous properties.
- Any clothing which becomes wet with liquid tetrahydrofuran should be removed immediately and not reworn until the tetrahydrofuran is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid tetrahydrofuran may contact the eyes.

SANITATION

- Skin that becomes wet with liquid tetrahydrofuran should be promptly washed or showered to remove any tetrahydrofuran.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetrahydrofuran may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in preparation of printing inks, adhesives, lacquers, and other coatings	General dilution ventilation; personal protective equipment
Use as a Grignard reagent in synthesis of motor fuels, vitamins, hormones, pharmaceuticals, synthetic perfumes, organometallic compounds and insecticides	General dilution ventilation; process enclosure; personal protective equipment
Use as an intermediate in the preparation of various chemicals, including adipic acid, butadiene, polytetramethylene, and acrylic acid	Process enclosure; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If tetrahydrofuran gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If tetrahydrofuran gets on the skin, promptly wash the contaminated skin with water. If tetrahydrofuran soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of tetrahydrofuran, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tetrahydrofuran has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tetrahydrofuran is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Tetrahydrofuran should

not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Tetrahydrofuran may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol, and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR TETRAHYDROFURAN

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20,000 ppm or less	A powered air-purifying respirator with a full facepiece and organic vapor cartridge(s). A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Tetramethyl Lead

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Pb(CH_3)_4$
- Synonyms: TML; lead tetramethyl; motor fuel anti-knock compound
- Appearance and odor: Colorless liquid (or dyed red, orange, or blue) with a slight musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetramethyl lead is 0.075 milligram of tetramethyl lead per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for tetramethyl lead a Threshold Limit Value of 0.150 mg/m^3 with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetramethyl lead can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Although there have been no reports of human intoxication from tetramethyl lead exposure, animal experiments suggest that tetramethyl lead may cause toxic effects similiar to those produced by tetraethyl lead. Tetraethyl lead exposure effects range from difficulty in sleeping, bad dreams, restlessness, anxiety, nausea, and poor appetite to the more severe symptoms of acute mental disturbance characterized by delirium, violent behavior, convulsive seizures, unconsciousness, and death. Fetal damage may occur from exposure of the mother to tetramethyl lead by analogy to methyl mercury.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetramethyl lead.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetramethyl lead at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of mental disorders or hypotension would be expected to be at increased risk from exposure. Examination of the central nervous system and the cardiovascular system should be stressed.

—Urinalysis: Normal kidney function is considered necessary for biologic monitoring. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The concentration of lead should be determined. Urine specimens with a specific gravity of less than 1.020 should be discarded and another sample obtained.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that the determination of the concentration of lead in the urine should be repeated quarterly.

- **Summary of toxicology**

Tetramethyl lead affects the central nervous system in animals and causes signs of increased irritability. Oral administration of 108 mg/kg to rats caused some deaths; effects were tremors, marked hyperactivity, and convulsions. Tetramethyl lead intoxication in animals resembles that caused by tetraethyl lead (TEL), a close

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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homolog; human intoxication from tetramethyl lead has not been described. A description of human intoxication by TEL is given because of the severity of the effects and the likelihood that intoxication by tetramethyl lead would be similar. TEL effects range from insomnia, bad dreams, restlessness, anxiety, hypotension, nausea, and anorexia to the more severe symptoms of acute mental disturbances characterized by delirium, mania, convulsive seizures, and coma, sometimes followed by death.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 267.3
2. Boiling point (760 mm Hg): 110 C (230 F)
3. Specific gravity (water = 1): 1.99
4. Vapor density (air = 1 at boiling point of tetramethyl lead): 6.5
5. Melting point: −30 C (−22 F)
6. Vapor pressure at 20 C (68 F): 22 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 100 C (212 F) cause decomposition and development of pressure that may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers, such as sulfuryl chloride or potassium permangonate, may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as lead fumes and carbon monoxide) may be released in a fire involving tetramethyl lead.
4. Special precautions: Tetramethyl lead will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 38 C (100 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of tetramethyl lead.
2. Eye Irritation Level: Tetramethyl lead is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of tetramethyl lead, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for tetramethyl lead is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with undiluted liquid tetramethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon).
- Clothing contaminated with undiluted liquid tetramethyl lead or solutions containing more than 1.06 milliliters liter (4 milliliters per gallon) of tetramethyl lead should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetramethyl lead from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetramethyl lead, the person performing the operation should be informed of tetramethyl lead's hazardous properties.
- Where there is any possibility of exposure of an

employee's body to undiluted liquid tetramethyl lead or solutiocontaining more than 1.06 milliliters per liter (4 milliliters per gallon) of tetramethyl lead, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with undiluted liquid tetramethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon) of tetramethyl lead should be removed immediately and not reworn until the tetramethyl lead is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid tetramethyl lead may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetramethyl lead may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture in preparation of antiknock fluids	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during formulation at petroleum refinery for use as an antiknock fluid; mixed lead alkyls; as substitutes, in whole or in part, for tetraethyl lead in engine gasoline	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid tetramethyl lead or strong concentrations of tetramethyl lead vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid tetramethyl lead or strong concentrations of tetramethyl lead vapors get on the skin, immediately rinse the contaminated skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. If liquid tetramethyl lead or strong concentrations of tetramethyl lead vapors penetrate through the clothing, remove the clothing immediately and first rinse the skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of tetramethyl lead, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tetramethyl lead has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tetramethyl lead is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Tetramethyl lead should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of tetramethyl lead vapors are permitted.

- Waste disposal method:

Tetramethyl lead may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR TETRAMETHYL LEAD

Condition	Minimum Respiratory Protection* Required Above 0.075 mg/m³
Vapor Concentration	
0.7 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3.5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of tetramethyl lead; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 40 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

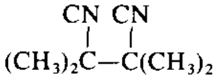
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TETRAMETHYL SUCCINONITRILE

INTRODUCTION

This guideline summarizes pertinent information about tetramethyl succinonitrile (TMSN) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_8H_{12}N_2$
- **Structure:**



$$(CH_3)_2\overset{\overset{CN}{|}}{C}-\overset{\overset{CN}{|}}{C}(CH_3)_2$$

- **Synonyms:** Succinonitrile tetramethyl, TMSN, TSN, tetramethyl-butanedinitrile
- **Identifiers:** CAS 3333-52-6; RTECS WN4025000; DOT Not assigned
- **Appearance and odor:** Colorless and odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 136.22
2. Specific gravity (water = 1): 1.07
3. Melting point: 170°C (338°F), sublimes
4. Insoluble in water

- **Reactivity**

1. Incompatibilities: Strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., cyanides, oxides of nitrogen, and carbon monoxide) may be released in a fire involving TMSN.

- **Flammability**

1. Extinguishant: Water, dry chemical, or carbon dioxide.
2. Caution: TMSN is a combustible solid. All ignition sources must be controlled when TMSN is used, handled, or stored so as not to create a potential fire or explosion hazard.

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, TMSN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TMSN is 0.5 parts of TMSN per million parts of air (ppm) [3.0 milligrams of TMSN per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 1 ppm (6 mg/m^3) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (3 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for tetramethyl succinonitrile

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	0.5	3
NIOSH REL ceiling (15 min)	1	6
ACGIH TLV® TWA (Skin)	0.5	3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

TMSN may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

Effects on animals: Acute inhalation, subcutaneous injection, or oral administration of TMSN to rats, mice, or hamsters

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produced severe convulsions and death within several hours of exposure.

- **Signs and symptoms of exposure**

Short-term (acute): Exposure to TMSN can cause headache, sensation of pressure within the head, dizziness, nausea, vomiting, peculiar taste, respiratory distress, fatigue, convulsions, and unconsciousness.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to TMSN, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to TMSN at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical findings consistent with a convulsant disorder.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to TMSN. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the central nervous system as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of TMSN. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting TMSN vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure TMSN may also be used if available. A detailed sampling and analytical method for TMSN may be found in the *NIOSH Manual of Analytical Methods* (method number S155).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with solid TMSN or liquids containing TMSN.

Workers should be provided with and required to use dust- and splash-proof safety goggles where TMSN may come in contact with the eyes.

SANITATION

Clothing which is contaminated with TMSN should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of TMSN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of TMSN's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with TMSN should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle TMSN should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to TMSN may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for tetramethyl succinonitrile

Operations	Controls
During the manufacture of polymers initiated by azobisisobutyronitrile; during the processing of products expanded with azobisisobutyronitrile	Local exhaust ventilation
During the manufacture of expanded polyvinyl chloride and polystyrene when azobisisobutyronitrile is used as a blowing agent	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to TMSN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If TMSN gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to TMSN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If TMSN gets on the skin, wash it immediately with soap and water. If TMSN penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If TMSN is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing TMSN, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from TMSN vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing TMSN may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. TMSN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in the solid form, TMSN may be collected and placed in an appropriate container.
6. TMSN solid or liquid may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for tetramethyl succinonitrile

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator Any self-contained breathing apparatus
Planned or emergency entry into environments containing unknown concentrations or levels above 5 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (6 mg/m^3) (ceiling).

Occupational Health Guideline for Tetranitromethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C(NO_2)_4$
- Synonyms: Tetan
- Appearance and odor: Colorless to pale yellow liquid or solid. The vapor has a pungent odor and causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetranitromethane is 1 part of tetranitromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 8 milligrams of tetranitromethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetranitromethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to tetranitromethane may cause irritation of the eyes, upper respiratory tract and skin. It may also cause headaches, fatigue, and drowsiness. After prolonged exposure, the central nervous system and heart may be affected and difficult breathing may occur. Tetranitromethane has been reported to affect the ability of the blood to carry oxygen. This may result in a bluish discoloration of the skin, headache, weakness, irritability, drowsiness, shortness of breath, and unconsciousness.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetranitromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetranitromethane at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory tract, eyes, blood, central nervous system, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Tetranitromethane causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Tetranitromethane is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—A complete blood count: Tetranitromethane has been shown to cause methemoglobinemia in humans. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematroccrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Tetranitromethane vapor is a severe irritant of the eyes and respiratory tract. The LC50 for rats was 1230 ppm

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for 36 minutes; effects were lacrimation, rhinorrhea, gasping, and cyanosis; pulmonary edema was present at autopsy. Repeated exposure to 3.65 ppm for 6 months caused the death of 60% of the rats; at autopsy there were signs of lung infection following acute pneumonitis. In three species of animals, intravenous injection caused methemoglobinemia, anemia, damage to the central nervous system, and edema of the lungs and liver. In workers, various studies showed that exposure caused irritation of the eyes, nose, and throat; dizziness, headache; chest pain, dyspnea; and occasionally skin irritation. Methemoglobinemia is stated to be a systemic effect from human exposure; symptoms result from anoxia and include cyanosis, evident especially in the lips, nose, and earlobes; other effects are weakness, dizziness, and severe headache. Concentrations in excess of 1 ppm will cause lacrimation and upper respiratory irritation, while 0.4 ppm may cause mild irritation. The liquid on the skin may cause mild burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 196
2. Boiling point (760 mm Hg): 126 C (259 F)
3. Specific gravity (water = 1): 1.64
4. Vapor density (air = 1 at boiling point of tetranitromethane): 6.8
5. Melting point: 14 C (57 F)
6. Vapor pressure at 20 C (68 F): 8.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Combustible organic matter wet with tetranitromethane may be highly explosive and susceptible to initiation by rather mild shocks.
2. Incompatibilities: Contact with hydrocarbons, alkalies, and metals may form explosive mixtures.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving tetranitromethane or when tetranitromethane decomposes.
4. Special precautions: Tetranitromethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible by itself, but is considered by some to be a weak explosive.

- **Warning properties**

1. Odor Threshold: Patty states that "tetranitromethane can be recognized by its characteristic acrid biting odor." No quantitative information is available, however, concerning its odor threshold.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the irritant property of tetranitromethane may serve as an index to the degree of exposure which can be tolerated, because concentrations in excess of 1 ppm will cause lacrimation and upper respiratory irritation. Concentrations as low as 0.4 ppm may cause mild irritation." Grant states that "the vapors of tetranitromethane are very irritating to the eyes, nose, and respiratory passages. It has been proposed for use as an irritant war gas. Animals are said to show evidence of irritation of the eyes rather quickly at concentrations from 3.3 to 25.2 ppm in air."
3. Evaluation of Warning Properties: Through its irritant effects, tetranitromethane can be detected below the permissible exposure limit. For the purposes of this guideline, therefore, tetranitromethane is treated as a material with good warning properties. It is a strong oxidizer.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by drawing tetranitromethane through ethyl acetate with subsequent gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure tetranitromethane may be used. An analytical method for tetranitromethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with solid or liquid tetranitromethane where skin contact may occur.
- Clothing which may have become contaminated with tetranitromethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetranitromethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetranitromethane, the person performing the operation should be informed of tetranitromethane's hazardous properties.
- Non-impervious clothing which becomes contaminated with tetranitromethane should be removed promptly and any clothing which becomes wet with liquid tetranitromethane should be removed immediately and not reworn until the tetranitromethane is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid tetranitromethane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid tetranitromethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with tetranitromethane should be promptly washed or showered with soap or mild detergent and water to remove any tetranitromethane.
- Eating and smoking should not be permitted in areas where tetranitromethane is handled, processed, or stored.
- Employees who handle solid or liquid tetranitromethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetranitromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as an ingredient in manufacture of liquid explosives; use as an octane number improver in diesel fuels	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory analytical reagent as a nitrating agent; use in research in rocket propellants	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid or liquid tetranitromethane or strong concentrations of tetranitromethane vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention promptly. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid or liquid tetranitromethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid tetranitromethane or penetrates through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of tetranitromethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solid or liquid tetranitromethane have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tetranitromethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material. Avoid shock and friction if liquid spills on combustible matter such as wood and paper.

- Waste disposal method:

Liquid tetranitromethane may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill. Solid tetranitromethane may be collected in the most convenient manner and disposed of in a secured sanitary landfill. Care should be taken when disposing, since tetranitromethane is a weak explosive.

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RESPIRATORY PROTECTION FOR TETRANITROMETHANE

Condition	**Minimum Respiratory Protection* Required Above 1 ppm**
Vapor Concentration	
5 ppm or less	Any chemical cartridge respirator with a full facepiece and a cartridge containing non-combustible sorbents and providing protection against tetranitromethane. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against tetranitromethane. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A gas mask containing non-combustible sorbents and providing protection against tetranitromethane. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Tetryl

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(NO_2)_3C_6H_2N(NO_2)CH_3$
- Synonyms: 2,4,6-trinitrophenylmethylnitramine; N-methyl-N,2,4,6-tetranitroaniline; nitramine; tetralite
- Appearance and odor: Colorless to yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetryl is 1.5 milligrams of tetryl per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetryl can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to tetryl may cause irritation of the eyes, nose, and throat. It may stain the skin and hair yellow. It may cause an allergic skin rash. Several days' exposure to high concentrations may cause headaches and nose bleeding. Occasionally, coughing and choking occur. Severe prolonged exposure may cause insomnia, nausea, vomiting, irritability, and anemia. In animals, it has caused liver and kidney damage, and severe breathing difficulties which may be delayed in onset.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetryl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetryl at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to tetryl may be at increased risk from exposure. Examination of the respiratory tract, eyes, liver, central nervous system, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Tetryl has been shown to cause anemia in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Tetryl dust causes severe sensitization dermatitis and irritation of the upper respiratory tract. Dogs injected subcutaneously with fatal doses showed degeneration of renal tubules, liver necrosis, and occasional pulmonary edema. Dermatitis in workers appears as early as the first week of exposure to the dust with itching of the eyes; there is a progression to erythema and edema occurring most often on the nasal folds, cheeks, and neck; papules and vesicles may develop; the remainder of the body is rarely affected. The severest forms show massive generalized edema with partial obstruction of the trachea due to swelling of the tongue and require

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hospitalization; exfoliation usually occurs after the edema subsides. The majority of these effects occur between the 10th and 20th days of exposure; upon cessation of exposure there is rapid abatement of the mild symptoms, and after 3 to 10 days disappearance of physical signs. Contact with tetryl causes a bright yellow staining, most often seen on the palms, face, neck, and in the hair. The irritant effects on the upper respiratory tract range from the nares to the bronchi and cause burning, itching, sneezing, coryza, epistaxis, and cough; the symptoms may begin the first day of exposure or as late as the third month; upon removal from exposure the symptoms regress over 2 to 4 weeks. Other effects reported in tetryl workers are irritability, easy fatigability, malaise, headache, lassitude, insomnia, nausea, and vomiting. Anemia, either of the marrow depression or deficiency type, has been observed among tetryl workers. Conjunctivitis may be caused by rubbing the eyes with contaminated hands or by airborne dust; keratitis and iridocyclitis have occurred.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 287
2. Boiling point (760 mm Hg): 187 C (369 F) (explodes)
3. Specific gravity (water = 1): 1.6 – 1.7
4. Vapor density (air = 1 at boiling point of tetryl): Not applicable
5. Melting point: 129 C (264 F)
6. Vapor pressure at 20 C (68 F): Much less than 1
7. Solubility in water, g/100 g water at 20 C (68 F): 0.02
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and shock
2. Incompatibilities: Contact of tetryl with some oxidizable materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving tetryl.
4. Special precautions: Protect from shock

- **Flammability**

1. Flash point: Explodes
2. Flammable limits in air, % by volume: Not applicable
3. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): 26 cm
4. Explosion temperature (temperature required to cause explosion in five seconds): 257 C (495 F)
5. Extinguishant: Water may be used on small fires. Do not attempt to extinguish large fires.

- **Warning properties**

Concerning the effects of tetryl on the eye, Grant states that "conjunctivitis may be caused by rubbing the eyes with contaminated hands, but more commonly airborne dust is responsible. Conjunctivitis is usually accompanied by dermatitis of the face, but may persist considerably longer than the skin rash. Keratitis and iridocyclitis are also said to have occurred in association with the conjunctivitis." No quantitative information is available concerning what concentrations in air produce the conjunctivitis, however.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of tetryl on a cellulose membrane filter with subsequent extraction with N,N-diethylethanolamine and spectrophotometric analysis. An analytical method for tetryl is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent repeated or prolonged skin contact with tetryl or liquids containing tetryl.

- If employees' clothing may have become contaminated with tetryl, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with tetryl should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetryl from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetryl, the person performing the operation should be informed of tetryl's hazardous properties.
- Non-impervious clothing which becomes contaminated with tetryl should be removed promptly and not reworn until the tetryl is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where tetryl or liquids containing tetryl may contact the eyes.

SANITATION

- Workers subject to skin contact with tetryl should wash any areas of the body which may have contacted tetryl at the end of each work day.
- Skin that becomes contaminated with tetryl should be promptly washed or showered with soap or mild detergent and water to remove any tetryl.
- Eating and smoking should not be permitted in areas where tetryl is handled, processed, or stored.
- Employees who handle tetryl or liquids containing tetryl should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetryl may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of explosives for use in blasting caps, boosters in high explosive shells, aircraft cannons, shells, and as a primer for less sensitive explosives; use during the formulation of binary explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a pH indicator	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If tetryl or liquids containing tetryl get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If tetryl or liquids containing tetryl get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tetryl or liquids containing tetryl penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of tetryl, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tetryl or liquids containing tetryl have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If tetryl is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. Attempt to reclaim spilled material; however, do not sweep or burn unless this is supervised by explosives experts.

- Waste disposal method:

Tetryl may be disposed of only by explosives experts.

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RESPIRATORY PROTECTION FOR TETRYL

Condition	Minimum Respiratory Protection* Required Above 1.5 mg/m³
Particulate Concentration	
7.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
15 mg/m³ or less	Any dust and mist respirator, except single-use respirator or quarter mask.** Any fume respirator or high efficiency particulate filter respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
75 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1500 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
3000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Soluble Thallium Compounds

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble thallium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

- Names and Formulas: 1) Thallium sulfate: Tl_2SO_4; 2) Thallium acetate: $TlC_2H_3O_2$; 3) Thallium nitrate: $TlNO_3$
- Appearance and odor: Thallium sulfate, thallium acetate, and thallium nitrate are all colorless, odorless solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble thallium compounds is 0.1 milligram of soluble thallium compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble thallium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin, or if they are swallowed. They may enter the body thorugh the skin.

- **Effects of overexposure**

Soluble thallium compounds are very toxic and cause cumulative intoxication. Many deaths have resulted from swallowing these compounds. Poisoning from industrial exposure has been rarely reported — those that have, were not fatal. Swallowing soluble thallium compounds may cause nausea, vomiting, diarrhea, abdominal pain, and bleeding from the gut. These symptoms are followed or accompanied by drooping of the eyelids, crossed eyes, weakness, numbness, and tingling of the arms and legs, trembling, and pain and tightness of the chest. The hair may fall out after two to three weeks. Severe intoxication may result in prostration, rapid heartbeat, convulsions, and psychosis. Recovery may be complete but permanent effects such as staggering, visual difficulties, trembling, and mental abnormalities have been reported. Liver and kidney damage have occurred. Repeated exposure over a prolonged period may produce variable symptoms. These may include loss of hair, soreness of the mouth, trembling, severe weight loss, and emotional disturbance.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble thallium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble thallium compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, nervous system, lungs, liver, kidneys, gastrointestinal tract, and body hair should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to thallium, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

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2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Soluble thallium compounds are extremely toxic and cause a cumulative intoxication affecting primarily the nervous system and the body hair. Many deaths have resulted from ingestion. The lethal oral dose of thallium acetate for humans is estimated to be about 12 mg/kg body weight. Ingestion causes nausea, vomiting, diarrhea, abdominal pain and gastrointestinal hemorrhage, which usually occur within 1 to 3 days. These are followed or accompanied by ptosis, strabismus; peripheral neuritis, pain, weakness, and paresthesias in the legs, tremor; retrosternal tightness and chest pain. Severe alopecia usually occurs after 2 to 3 weeks and is pathognomonic of the toxic effects of thallium. Severe intoxication may result in prostration, tachycardia, blood pressure fluctuations, convulsive seizures, choreaform movements, and psychosis. Recovery may be complete, but permanent residual effects such as ataxia, optic atrophy, tremor, mental abnormalities, and footdrop have been reported. In cases of fatal intoxication, typical autopsy findings include pulmonary edema, necrosis of the liver, nephritis, and degenerative changes in peripheral axons. Prolonged ingestion of thallium produces a variable clinical picture which includes stomatitis, tremor, cachexia, polyneuropathy, alopecia, and emotional disturbance. In a study of 15 workers who had handled solutions of organic thallium salts over a 7.5-year period, 6 workers suffered thallium intoxication; chief complaints were abdominal pain, fatigue, weight loss, pain in the legs, and nervous irritability; 3 of the workers had albuminuria and 1 had hematuria.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

These data correspond to the the three substances identified above.

1. Molecular weight: 1) 504.81; 2) 263.41; 3) 266.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1) 6.8; 2) 3.7; 3) 5.5
4. Vapor density (air = 1 at boiling point of soluble thallium compounds): Not applicable
5. Melting point: 1) 632 C (1170 F); 2) 110 C (230 F); 3) 206 C (403 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 1) 4.87; 2) Very soluble; 3) 10
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: None.
3. Hazardous decomposition products: None.
4. Special precautions: None.

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Water, carbon dioxide, foam, dry chemical

- **Warning properties**

Grant describes some effects on the eye produced by systemic thallium poisoning. In addition, Grant states that "experiments concerned with the local effects of thallium on the eye suggest that contact of thallium salts with the eye, such as by accidental splash contamination, is unlikely to cause serious damage, especially if promptly washed away with water. Experimentally, a rather drastic exposure of a rabbit eye for ten minutes to a neutral saturated solution of thallium chloride, with the epithelium preliminarily removed to facilitate penetration, caused moderate edema and haze in the cornea, which gradually cleared from the periphery but left a nebulous area axially. Splash contact with intact epithelium presumably would be even less damaging."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a filter with a subsequent atomic absorption spectrophotometric analysis. An analytical method for soluble thallium compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted

are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with soluble thallium compounds where skin contact may occur.
- If employees' clothing may have become contaminated with soluble thallium compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with soluble thallium compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of soluble thallium compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the soluble thallium compounds, the person performing the operation should be informed of soluble thallium compounds's hazardous properties.
- Non-impervious clothing which becomes contaminated with soluble thallium compounds should be removed promptly and not reworn until the soluble thallium compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble thallium compounds may contact the eyes.

SANITATION

- Skin that becomes contaminated with soluble thallium compounds should be promptly washed or showered to remove any soluble thallium compounds.
- Eating and smoking should not be permitted in areas where soluble thallium compounds are handled, processed, or stored.
- Employees who handle soluble thallium compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble thallium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Use in laboratory for analytical and research purposes	Local exhaust ventilation; personal protective equipment
Use in manufacture of special lenses, plates and prisms, medicinals, pyrotechnic products, and fuel additives for internal combustion engines	Local exhaust ventilation; personal protective equipment
Manufacture of soluble thallium compounds and application as a rodenticidal agent	Local exhaust ventilation; personal protective equipment; product substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If soluble thallium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If soluble thallium compounds get on the skin, promptly flush the contaminated skin with water. If soluble thallium compounds penetrate through the clothing, remove the clothing promptly and flush the skin with water. Get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble thallium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble thallium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble thallium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in a sealed container for disposal. Large quantities may be reclaimed; however, if this is not practical, collect spilled material in the most convenient and safe manner and deposit in sealed containers for disposal.
3. Liquids containing soluble thallium compounds may be absorbed in vermiculite, dry sand, earth, or a similar material and deposited in sealed containers for disposal.

- Waste disposal method

Soluble thallium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOLUBLE THALLIUM COMPOUNDS

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m³**
Dust or Mist Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
1 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A powered air-purifying respirator with a full facepiece, helmet, or hood, and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Thiram

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_{12}N_2S_4$
- Synonyms: Tetramethylthiuram disulfide
- Appearance: Colorless to cream solid (some commercial products are dyed blue).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for thiram is 5 milligrams of thiram per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Thiram can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Thiram can cause irritation of the eyes, nose, throat, and skin. It may cause an allergic skin rash. Thiram is thought to have similar effects as antabuse which include nausea, vomiting, diarrhea, and loss of appetite. After ingestion of alcohol, individuals taking antabuse may experience skin redness, hives, itching, pulsating headache, flushing, sweating, nausea, vomiting, diarrhea, weakness, dizziness, and difficulty in breathing. Thiram has caused birth defects in offspring of animals given large doses of thiram by mouth.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to thiram.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to thiram at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from thiram exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of thiram might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Thiram is a skin sensitizer. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Thiram (tetramethylthiuram disulfide) dust irritates the respiratory tract, eyes, and skin, and causes sensitization dermatitis. Thiram was teratogenic (skeletal malformations) in hamsters given a single oral dose of 250 mg/kg during the period of organogenesis and in mice given oral doses of 5 to 30 mg/animal daily between days 6 and 17 of pregnancy. In exposed humans, sensitization dermatitis in the form of eczema has occurred on the hands, forearms, and feet. Thiram is thought to have similar toxic effects to antabuse, which include nausea, vomiting, diarrhea, and loss of appetite. Ingestion of ethanol by persons taking antabuse has caused a severe reaction characterized by a rapid skin response of a nonallergic nature, flushing, erythema, pruritis, urticaria, headache, nausea, vomiting, diarrhea, weakness, dizziness, and difficult breathing.

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Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 240
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.40
4. Vapor density (air = 1 at boiling point of thiram): Not applicable
5. Melting point: 140 C (284 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids or oxidizable materials may cause formation of toxic gases such as hydrogen sulfide.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, carbon disulfide, and carbon monoxide) may be released in a fire involving thiram.
4. Special precautions: None

- **Flammability**

1. Flash point: 89 C (192 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, foam, dry chemical

- **Warning properties**

Warning properties are not considered since the vapor pressure is negligible.

Grant states that "as a dust or spray it is irritating to the eyes . . . ." No quantitative information is available concerning the eye irritation threshold, however.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of thiram on a membrane filter with subsequent chemical treatment and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure thiram may be used. An analytical method for thiram is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with thiram or liquids containing thiram, where skin contact may occur.
- If employees' clothing may have become contaminated with solid thiram, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with thiram should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of thiram from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the thiram, the person performing the operation should be informed of thiram's hazardous properties.
- Non-impervious clothing which becomes contaminated with thiram should be removed promptly and not reworn until the thiram is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where thiram or liquids containing thiram may contact the eyes.

SANITATION

- Skin that becomes contaminated with thiram should be promptly washed or showered with soap or mild detergent and water to remove any thiram.
- Eating and smoking should not be permitted in areas where thiram is handled, processed, or stored.

- Employees who handle thiram or liquids containing thiram should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to thiram may occur and control methods which may be effective in each case:

Operation	Controls
Use in rubber industry as an accelerator, peptizing agent, and vulcanizing agent	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during application as an agricultural fungicide as foliage spray for plants and trees, fruits and seeds	Handle mechanically; personal protective equipment
Use as a bacteriostat in commercial and surgical soap, antiseptics, sunburn oils and fats	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use as an animal repellant on plants or trees	Handle mechanically; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If thiram or liquids containing thiram get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If thiram or liquids containing thiram get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If thiram or liquids containing thiram penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Swallowing**

When thiram or liquids containing thiram have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If thiram is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Thiram may be disposed of:

1. By making packages of thiram in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving thiram in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR THIRAM

Condition	**Minimum Respiratory Protection* Required Above 5 mg/m^3**
Particulate Concentration	
50 mg/m^3 or less	Any supplied-air respirator. Any self-contained breathing apparatus. Any pesticide chemical cartridge respirator.
250 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. Any pesticide chin-style cartridge respirator with a full facepiece. A chin-style or a front- or back-mounted pesticide gas mask.
1500 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying pesticide respirator with a full facepiece, helmet, or hood.
Greater than 1500 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Inorganic Tin Compounds (as Tin)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all inorganic tin compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Tin

- Formula: Sn
- Synonyms: Tin, metallic
- Appearance and odor: Odorless, dull silvery metal.

Stannous chloride

- Formula: $SnCl_2$
- Synonyms: Tin(II) chloride; tin dichloride
- Appearance and odor: Odorless, colorless to brown solid.

Stannic chloride

- Formula: $SnCl_4$
- Synonyms: Tin(IV) chloride; tin tetrachloride
- Appearance and odor: Colorless to yellow fuming liquid with an acrid odor.

Stannous sulfate

- Formula: $SnSO_4$
- Synonyms: Tin(II) sulfate
- Appearance and odor: Odorless, colorless to brown solid.

Potassium stannate

- Formula: $K_2SnO_3 3H_2O$
- Synonyms: Potassium stannate trihydrate
- Appearance and odor: Odorless, colorless to brown solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for inorganic tin compounds (as tin) is 2 milligrams of inorganic tin compounds (as tin) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tin, stannous chloride, stannic chloride, stannous sulfate, or potassium stannate can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: In general, the toxicity of inorganic tin salts is low. These compounds may cause irritation of the eyes, nose, throat, and skin.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to inorganic tin compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to inorganic tin compounds at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from inorganic tin compounds exposure.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Skin disease: Certain inorganic tin compounds other than oxides are primary skin irritants. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of certain inorganic tin compounds might cause exacerbation of symptoms due to their irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Inorganic tin compounds (except the oxides) irritate the eyes and skin. Subcutaneous injection of animals with sodium stannous tartrate at a daily dose of 12.5 mg/kg was fatal; death was preceeded by vomiting, diarrhea, and paralysis with twitching of the limbs. Daily administration to a dog of stannous chloride in milk at a level of 500 mg/kg produced paralysis after 14 months. Some inorganic tin compounds can cause skin or eye irritation because of acid or alkaline reaction produced with water; tin tetrachloride, stannous chloride, and stannous sulfate are strong acids; sodium and potassium stannate are strong alkalis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Tin**

1. Molecular weight: 118.7
2. Boiling point (760 mm Hg): 2689 C (4873 F)
3. Specific gravity (water = 1): 5.8 to 7.3
4. Vapor density (air = 1 at boiling point of tin): Not applicable
5. Melting point: 232 C (450 F)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Stannous chloride**

1. Molecular weight: 189.6
2. Boiling point (760 mm Hg): 605 C (1121 F)
3. Specific gravity (water = 1): 3.95
4. Vapor density (air = 1 at boiling point of stannous chloride): Not applicable
5. Melting point: 247 C (477 F)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 90
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Stannic chloride**

1. Molecular weight: 260.5
2. Boiling point (760 mm Hg): 114 C (237 F)
3. Specific gravity (water = 1): 2.23
4. Vapor density (air = 1 at boiling point of stannic chloride): 9
5. Melting point: −33 C (−27 F)
6. Vapor pressure at 20 C (68 F): 18 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Stannous sulfate**

1. Molecular weight: 214.8
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available (greater than 1)
4. Vapor density (air = 1 at boiling point of stannous sulfate): Not applicable
5. Melting point: 300 C (572 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Potassium stannate**

1. Molecular weight: 298.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.2
4. Vapor density (air = 1 at boiling point of potassium stannate): Not applicable
5. Melting point: 140 C (284 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 110
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: If moisture enters containers of stannic chloride, pressure may burst containers. At temperatures above 360 C (680 F), stannous sulfate decomposes to form toxic sulfur dioxide.
2. Incompatibilities: Contact of metallic tin with chlorine may cause adjacent combustible material to ignite. Contact of metallic tin with turpentine may cause fires and explosions. Contact of stannic chloride with water, alcohols, and amines may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving the tin chlorides and stannous sulfate.
4. Special precautions: Stannic chloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: a) Tin: 630 C (1166 F) (cloud); 430 C (806 F) (layer); For the other compounds: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For tin, water; for the other compounds, not applicable.

- **Warning properties**

According to Grant, tin tetrachloride (stannic chloride) is "highly irritating to the eyes and mucous membranes.

The irritation presumably is attributable to the hydrochloric acid which is generated when stannic chloride reacts with water." The threshold of eye irritation is not given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by treatment with nitric and sulfuric acids, solution in hydrochloric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for inorganic tin compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid stannic chloride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with stannous sulfate, potassium stannate, or liquids containing these compounds, where skin contact may occur.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with stannous chloride or liquids containing stannous chloride.
- If employees' clothing may have become contaminated with solid stannous chloride, stannous sulfate, or potassium stannate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with stannous chloride, stannic chloride, stannous sulfate, or potassium stannate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid stannic chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where exposure of an employee's body to stannous sulfate, potassium stannate, or liquids containing these compoumay occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with stannic chloride, stannous sulfate, or potassium stannate should be removed immediately and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes wet with stannous chloride should be removed promptly and not reworn until the stannous chloride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of liquid stannic chloride, stannous sulfate or liquids containing stannous sulfate, or potassium stannate or liquids containing potassium stannate contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where stannous chloride or liquids containing stannous chloride may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid stannic chloride, stannous sulfate or liquids containing stannous sulfate, or potassium stannate or liquids containing potassium stannate,

an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with stannic chloride, stannous sulfate, or potassium stannate should be immediately washed or showered to remove any contaminant.
- Skin that becomes wet with stannous chloride should be promptly washed or showered to remove any stannous chloride.
- Employees who handle stannous chloride, stannic chloride, stannous sulfate, or potassium stannate should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to inorganic tin compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, roasting, and smelting of cassiterite ore; during foundry operations and finishing operations	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of stannic chloride in dyeing silk; manufacture of blue-print paper; as a perfume stabilizer in soap; in the preparation of lubricating oil additives; in treating glass surfaces; as a catalyst in manufacture of pharmaceuticals; and as a bleaching agent for sugar	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of stannous chloride in acidic electrotinning baths; manufacture of blue-print paper; as an antisludge agent in lubricating oils; as a perfume stabilizer in soap; as a catalyst in organic reactions; as an additive in drilling mud; in silvering of mirrors; and as a food additive	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in production of stannous fluoride or stannous pyrophosphate for use tinning baths and for formulations for remineralization of teeth; use of stannous fluorborate in commercial tin-plating baths; use in production of sodium stannate	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in production of potassium stannate; use of stannous perchlorate in tin-plating solutions; use of stannic chromate as a ceramic pigment	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of tin hydride to gas-phase plate tin on metal and ceramic surfaces; use of stannous sulfide as a pigment, as a catalyst, and in manufacture of bearing materials	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in production of stannous sulfate for use in acidic electrotinning baths and in dyeing textiles	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of stannous oleate or stannous 2-ethyl hexoate as a catalyst for urethane and other polymer foams and as a fabric water-repellant	Personal protective equipment
Use of stannous acetate as a catalyst and agent to promote exhaustion of dyes	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use of heavy metal stannates as additives to ceramic dielectric materials	Process enclosure; local exhaust ventilation; personal protective equipment
Use of stannous tartrate in printing and dyeing of textiles	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

Use of stannous oxalate as a catalyst in esterification reactions and in coal hydrogenation; use of stannic bromide for metallurgical separation of minerals in the laboratory	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If tin, stannous sulfate, or potassium stannate get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If inorganic tin compounds get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If inorganic tin compounds penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of inorganic tin compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When inorganic tin compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If tin, stannous chloride, stannic chloride, stannous sulfate, or potassium stannate are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled or leaked material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing inorganic tin compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Inorganic tin compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR INORGANIC TIN COMPOUNDS (AS TIN)

Condition	**Minimum Respiratory Protection* Required Above 2 mg/m³**
Particulate Concentration	
10 mg/m³ or less	Any dust and mist respirator, except single-use.**
20 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume or high efficiency particulate filter respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
100 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
400 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 400 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Organic Tin Compounds (as Tin)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all organic tin compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Dibutyltin di-2-ethylhexoate

- Formula: $(C_4H_9)_2Sn(C_8H_{15}O_{2+}$
- Synonyms: Dibutyltin dioctoate
- Appearance and odor: Waxy solid with a weak odor.

Bis(tri-n-butyltin) oxide

- Formula: $((C_4H_9)_3Sn)_2O$
- Synonyms: TBTO
- Appearance and odor: Colorless to yellow liquid with a weak odor.

Triphenyltin chloride

- Formula: $(C_6H_5)_3SnCl$
- Synonyms: None
- Appearance and odor: Colorless to yellow solid with a characteristic odor.

Dibutyltin dichloride

- Formula: $(C_4H_9)_2SnCl_2$
- Synonyms: None
- Appearance: Light tan or colorless solid or semi-solid.

Dibutyltin diacetate

- Formula: $(C_4H_9)_2Sn(C_2H_3O_2)_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a weak vinegar odor.

Tetrabutyltin

- Formula: $(C_4H_9)_4Sn$
- Synonyms: Tetra-n-butyltin
- Appearance and odor: Colorless liquid with a distinct, characteristic odor.

Stannous 2-ethylhexoate

- Formula: $Sn(C_8H_{15}O_2)_2$
- Synonyms: Stannous octoate; tin octoate
- Appearance and odor: Pale yellow, viscous liquid with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for organic tin compounds is 0.1 milligram of organic tin compounds (as tin) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 0.1 milligram of tin per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Organotin Compounds should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Organic tin compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin.

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They can also affect the body if they are swallowed and they may be absorbed through the skin.

- **Effects of overexposure**

Little is known of the toxicity of monoalkyl tin compounds except that the toxicity of monoethyl tin chloride is low. Dialkyl tin compounds have caused irritation of the skin and damage to the liver and bile ducts in animals. This has resulted in animal deaths from liver failure and peritonitis. Swallowing diethyl tin has caused permanent damage to the nervous system and deaths in humans. Trialkyl and tetraalkyl tin compounds have caused nervous system damage in animals. Trialkyl and dibutyl tins have caused skin burns in humans. Tetramethyl and tetraethyl tin have caused headache and vomiting in humans. Tributyl tin compounds have caused severe skin burns in humans.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to organic tin compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to organic tin compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, eyes, liver, and urinary tract should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since some organic tin compounds may cause urinary retention, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Organic tin compounds cause hepatic necrosis in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—A complete blood count: Organic tin compounds cause hemolysis in animals. A complete blood count should be performed including a red cell count, a white cell count, a differential on a stained smear, as well as hemoglobin and hematocrit.

—Eye disease: Since some organic tin compounds may produce neurological damage, the eyes should be examined for such abnormalities as glaucoma and choked disc; general tests of visual acuity should be performed as well. In addition, evidence indicating past or present increased intracranial pressure should be evaluated.

—Cardiovascular system: An electrocardiogram should be performed on workers over 40 years of age and where indicated.

—Skin disease: Organic tin compounds are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The organic tin compounds, chiefly solids and liquids, cause irritation of the eyes, throat, and skin; some produce cerebral edema, while others cause hepatic necrosis. Oral administration of a preparation of organic tin containing diethyltin di-iodide and up to 10% triethyltin for treatment of human furunculosis resulted in 217 cases of poisoning, 100 of which were fatal. After a latent period of 4 days there was severe persistent headache followed by vertigo, visual disturbances including photophobia, abdominal pain, vomiting, and urinary retention; the more severe cases showed transient or permanent paralysis and psychic disturbances. Residual symptoms in those who recovered included persistent headache, diminished visual acuity, partial paresis, focal anesthesia, and in four severe cases, flaccid paraplegia with incontinence. The most significant lesion found at necropsy was cerebral edema. Repeated oral administration to rats of 50 mg/kg of dibutyltin chloride resulted in inflammation of bile ducts and hepatic necrosis; repeated skin applications of 10 mg/kg caused severe local skin injury and bile duct damage. Triethyltin sulfate administered repeatedly to rats at 10 mg/kg caused tremors and paresis, which in some animals progressed to complete paralysis and death; it was equally toxic by mouth and by injection. In mice, tributyltin chloride had a marked hemolytic action, while dibutyl and tetrabutyl tin were less markedly hemolytic. Workers exposed to the vapor or fume of butyltin compounds developed sore throat and cough several hours after exposure. Chemical burns from organic tin compounds may result from only brief contact with the skin; pain is usually moderate and itching is the chief symptom; healing is usually complete within 7 to 10 days. When a worker was splashed in the face with a tributyltin compound, lacrimation and severe conjunctivitis appeared within minutes, despite immediate lavage, and persisted for 4 days; at the end of 7 days the eyes appeared normal.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Dibutyltin di-2-ethylhexoate**

1. Molecular weight: 522.7
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.07
4. Vapor density (air = 1 at boiling point of dibutyltin di-2-ethylhexoate): Not applicable
5. Melting point: 54 C (129 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Bis(tri-n-butyltin) oxide**

1. Molecular weight: 595.4

2. Boiling point (760 mm Hg): 254 C (489 F) at 50 mm Hg

3. Specific gravity (water = 1): 1.17

4. Vapor density (air = 1 at boiling point of bis(tri-n-butyltin)oxide): Not applicable

5. Melting point: Data not available

6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Less than 20 ppm

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Triphenyltin chloride**

1. Molecular weight: 385.5

2. Boiling point (760 mm Hg): 240 C (464 F) at 13 mm Hg

3. Specific gravity (water = 1): Greater than 1

4. Vapor density (air = 1 at boiling point of triphenyltin chloride): Not applicable

5. Melting point: 106 C (223 F)

6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Dibutyltin dichloride**

1. Molecular weight: 303.8

2. Boiling point (760 mm Hg): 135 C (275 F) at 10 mm Hg

3. Specific gravity (water = 1): 1.36

4. Vapor density (air = 1 at boiling point of dibutyltin dichloride): Not applicable

5. Melting point: 43 C (109 F)

6. Vapor pressure at 20 C (68 F): 2 mm Hg/100 C (212 F)

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Dibutltin diacetate**

1. Molecular weight: 351

2. Boiling point (760 mm Hg): 144 C (291 F) at 10 mm Hg

3. Specific gravity (water = 1): 1.32

4. Vapor density (air = 1 at boiling point of dibutyltin diacetate): Not applicable

5. Melting point: 10 C (50 F)

6. Vapor pressure at 20 C (68 F): 1.3 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Tetrabutyltin**

1. Molecular weight: 347.2

2. Boiling point (760 mm Hg): 145 C (293 F) at 10 mm Hg

3. Specific gravity (water = 1): 1.06

4. Vapor density (air = 1 at boiling point of tetrabutyltin): Not applicable

5. Melting point: Less than −70 C (less than −94 F)

6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Slight

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Stannous 2-ethylhexoate**

1. Molecular weight: 404.7

2. Boiling point (760 mm Hg): Decomposes at 200 C (392 F)

3. Specific gravity (water = 1): 1.26

4. Vapor density (air = 1 at boiling point of stannous 2-ethylhexoate): Not applicable

5. Melting point: Less than −25 C (less than −13 F)

6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving organic tin compounds.

4. Special precautions: Organic tin compounds will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: a) Dibutyltin di-2-ethylhexoate: Data not available; b) Bis(tri-n-butyltin) oxide: Greater than 100 C (212 F); c) Triphenyltin chloride: Data not available; d) Dibutyltin dichloride: 168 C (334 F); e) Dibutyltin diacetate: 143 C (289 F); f) Tetrabutyltin: 124 C (255 F); g) Stannous 2-ethylhexoate: 142 C (287 F)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available (probably because too high boiling points)

4. Extinguishant: Water, foam, dry chemical, and carbon dioxide

- **Warning properties**

Concerning the toxicity of organic tin, Browning states "The eyes are rarely involved, but accidental splashing can cause lacrimation and intense suffusion of the conjunctiva which persists for several days, but with no permanent injury."

Grant lists several toxic effects produced by triethyltin on the eye, but these injuries are caused by systemic poisoning, not by a local effect on the eye.

The NIOSH Criteria Document cites Landa et al. as having observed eye and upper respiratory tract irritation from bis(tributyltin) oxide at an average air concentration of 0.05 mg/m^3 measured as tin, but noted that this concentration may not be entirely accurate since the limit of sensitivity of the measurement method used was 0.1 mg/m^3.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of organic tin compounds on a filter, followed by chemical treatment and subsequent spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure organic tin compounds may be used. An analytical method for organic tin compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with triphenyltin chloride or liquids containing triphenyltin chloride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with dibutyltin di-2-ethylhexoate or liquids containing dibutyltin di-2-ethylhexoate, liquid bis(tri-n-butyltin) oxide, solid or liquid dibutyltin diacetate, liquid tetrabutyltin, or liquid stannous 2-ethylhexoate.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with dibutyltin dichloride or liquids containing dibutyltin dichloride, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with solid triphenyltin chloride or dibutyltin dichloride, employees should change into uncontaminated clothing before leaving the work premises.
- If employees' clothing may have become contaminated with solid dibutyltin di-2-ethylhexoate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to triphenyltin chloride or liquids containing triphenyltin chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where exposure of an employee's body to dibutyltin dichloride or liquids containing dibutyltin dichloride may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with triphenyltin chloride or dibutyltin dichloride should be removed immediately and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide,dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of triphenyltin chloride or liquids containing triphenyltin chloride contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where dibutyltin di-2-ethylhexoate or liquids containing dibutyltin di-2-ethylhexoate, dibutyltin dichloride or liquids contain-

ing dibutyltin dichloride, liquid bis(tri-n-butyltin) oxide, solid or liquid dibutyltin diacetate, liquid tetrabutyltin, or liquid stannous 2-ethylhexoate may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to triphenyltin chloride or liquids containing triphenyltin chloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with triphenyltin chloride or dibutyltin dichloride should be immediately flushed with large amounts of water to remove any contaminant.
- Workers subject to skin contact with solid dibutyltin di-2-ethylhexoate, triphenyltin chloride, or dibutyltin dichloride should wash with soap or mild detergent and water any areas of the body which may have contacted any contaminant at the end of each work day.
- Skin that becomes contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.
- Eating and smoking should not be permitted in areas where dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin dichloride, dibutyltin diacetate, or tetrabutyltin are handled, processed, or stored.
- Employees who handle dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to organic tin compounds may occur and control methods which may be effective in each case:

Operation	Controls
Use as a stabilizing agent against degradation effects fo light, heat, and oxygen on poly vinyl chloride, neoprene, chlorinated polyethylenes, vinyl copolymers, silicones, and polyamides	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst in organic and inorganic synthesis in condensation, esterification, halogenation, hydrogenation, oxidation, and polymerization	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, bactericides, fungicides, and molluscides; use as U.S. Food and Drug-sanctioned chemical on agricultural crops	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of rodent repellants for wire cable	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as veterinary medicine as poultry anthelmintic	General dilution ventilation
Use as a fuel additive and lubricant	Process enclosure

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If organic tin compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate get on the skin, immediately flush with large amounts of water, then wash with soap or mild detergent and water. If dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate soak through the clothing, remove the clothing immediately and flush with large amounts of water and then wash using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of organic tin compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When organic tin compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If organic tin compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing organic tin compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Organic tin compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ORGANIC TIN COMPOUNDS (AS TIN)

Condition	**Minimum Respiratory Protection*** **Required Above 0.1 mg/m³**
Particulate Concentration	
1 mg/m³ or less	A chemical cartridge respirator with an organic vapor cartridge(s) and a dust and mist filter. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	Any chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and high efficiency filter (s). Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Titanium Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: TiO_2
- Synonyms: Rutile; anatase; brookite
- Appearance and odor: White powder with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for titanium dioxide is 15 milligrams of titanium dioxide (total dust) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for titanium dioxide a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Titanium dioxide can affect the body if it is inhaled.

- **Effects of overexposure**

Slight change in the lungs may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to titanium dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to titanium dioxide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from titanium dioxide exposure.

—Chronic respiratory disease: Titanium dioxide is a nuisance dust. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of titanium dioxide might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Titanium dioxide dust is a mild pulmonary irritant. Rats repeatedly exposed to concentrations of 10 to 328 million particles per cubic foot of air for as long as 13 months showed small focal areas of emphysema, which were attributed to large deposits of dust; there was no evidence of any specific lesion being produced by titanium dioxide. Three of 15 workers who had been exposed to titanium dioxide dust showed radiographic signs in the lungs resembling "slight fibrosis," but disabling injury did not occur; the magnitude and duration of exposure were not specified. In the lungs of three workers involved in processing titanium dioxide pigments, deposits of the dust in the pulmonary interstitium were associated with cell destruction and slight fibrosis; the findings indicated that titanium dioxide is a mild pulmonary irritant.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 79.9
2. Boiling point (760 mm Hg): Less than 3000 C (less than 5432 F)
3. Specific gravity (water = 1): 3.9 – 4.2
4. Vapor density (air = 1 at boiling point of titanium dioxide): Not applicable
5. Melting point: 1640 C (2984 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

According to Grant, titanium dioxide "is a white pigment which is insoluble in water and very inert. It has been introduced by tattooing into the corneas of rabbits and patients having corneal scars, and has caused permanent white coloration but no irritation." For the purposes of this guideline, therefore, titanium dioxide is not treated as an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of titanium dioxide on a filter, followed by treatment with nitric acid, solution by heating with sulfuric acid and ammonium sulfate, and atomic desorption spectrophotometric analysis. An analytical method for titanium dioxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4)

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to titanium dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining, purification, packaging, and distribution	General dilution ventilation; personal protective equipment
Use as a pigment in manufacture of paints, varnishes, and lacquers to impart whiteness, opacity, and brightness	General dilution ventilation; personal protective equipment
Use in manufacture of paper used in coatings and fillers to improve opacity and brightness; manufacture of paper, photographic papers, paper packaging, and cellophane coatings	General dilution ventilation; personal protective equipment
Use as a white pigment in manufacture of plastics; blow-molded plastic containers	General dilution ventilation; personal protective equipment
Use in manufacture of elastomers for use in tire sidewalls, footwear, floor mats, gloves, rainwear, and wall coverings; use in manufacture of floor coverings	General dilution ventilation; personal protective equipment
Use in manufacture of ceramics and glass for capacitors, electromechanical transducers, welding-rod coatings, and glass fibers	General dilution ventilation; personal protective equipment
Use in manufacture of printing inks for flexographic, gravure, and letter press inks; packaging, publication, offset, and screen processing inks	General dilution ventilation; personal protective equipment

Use in manufacture of coated fabrics and textiles on natural/artificial leather, oilcloth, upholstery materials, and wall coverings; as a delustrant for acrylic, nylon, and spandex fibers	General dilution ventilation; personal protective equipment
Use in manufacture of building materials in roofing granules, ceiling tiles, cement-curing aids, and titanium carbide cutting tools	General dilution ventilation; personal protective equipment
Use in manufacture of cosmetics, food color additives, and synthetic diamonds	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of titanium dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If titanium dioxide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing titanium dioxide should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Titanium dioxide may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR TITANIUM DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 15 mg/m^3
Dust or Mist Concentration	
75 mg/m^3 or less	Any dust and mist respirator.
150 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
150 mg/m^3 or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7,500 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7,5000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Toluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5CH_3$
- Synonyms: Toluol; phenylmethane; methylbenzene
- Appearance and odor: Colorless liquid with an aromatic odor, like benzene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for toluene is 200 parts of toluene per million parts of air (ppm) averaged over an eight-hour work shift, and during any such work shift, 300 ppm toluene may not be exceeded except that a peak of 500 ppm toluene is permitted for 10 minutes during the eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 100 ppm toluene averaged over an eight-hour work shift with a ceiling level of 200 ppm averaged over a ten-minute period. The NIOSH Criteria Document for Toluene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Toluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Toluene may cause irritation of the eyes, respiratory tract, and skin. It may also cause fatigue, weakness, confusion, headache, dizziness, and drowsiness. Peculiar skin sensation may be produced such as a "pins and needles feeling" or numbness. Very high concentrations may cause unconsciousness and death. The liquid splashed in the eye may cause irritation and temporary damage. Inhalation may also cause difficulty in seeing in bright light. If liquid toluene is splashed in the eyes, it will cause temporary irritation.

2. Long-term Exposure: Repeated or prolonged exposure to liquid toluene may cause drying and cracking of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to toluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to toluene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since proper kidney function is necessary for biologic monitoring, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be analyzed for hippuric acid to obtain a background level.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Hippuric acid level in urine may be an indicator of the level of toluene exposure.

- **Summary of toxicology**

Toluene vapor causes narcosis. Controlled exposure of human subjects to 200 ppm for 8 hours produced mild fatigue, weakness, confusion, lacrimation, and paresthesia; at 600 ppm for 8 hours there were also euphoria, headache, dizziness, dilated pupils and nausea; at 800

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ppm for 8 hours, symptoms were more pronounced, and after-effects included nervousness, muscular fatigue, and insomnia persisting for several days. Severe but reversible liver and kidney injury occurred in a person who was a glue-sniffer for 3 years; the chief component of the inhaled solvent was toluene (80% V/V); other ingredients were not listed. In workers exposed for many years to concentrations in the range of 80 to 300 ppm, there was no clinical or laboratory evidence of altered liver function. Toluene exposure does not result in the hematopoietic effects caused by benzene; the myelotoxic effects previously attributed to toluene are judged by more recent investigations to be the result of concurrent exposure to benzene present as a contaminant in the commercial toluene used. Most of the toluene absorbed from inhalation is metabolized to benzoic acid, conjugated with glycine in the liver to form hippuric acid, and excreted in the urine; the average amount of hippuric acid excreted in the urine by individuals not exposed to toluene is approximately 0.7 to 1.0 g/l of urine. The liquid splashed in the eyes of two workers caused transient corneal damage and conjunctival irritation; complete recovery occurred within 48 hours. Repeated or prolonged skin contact with liquid toluene has a defatting action, causing drying, fissuring, and dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 92.1
2. Boiling point (760 mm Hg): 111 C (231 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of toluene): 3.14
5. Melting point: −95 C (−139 F)
6. Vapor pressure at 20 C (68 F): 22 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.05
8. Evaporation rate (butyl acetate = 1): 2.24

- **Reactivity**

1. Conditions contributing to instability: Containers may burst at elevated temperatures.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon dioxide and carbon monoxide) may be released in a fire involving toluene.
4. Special precautions: Toluene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 4 C (40 F) (closed cup)
2. Autoignition temperature: 480 C (896 F)
3. Flammable limits in air, % by volume: Lower: 1.27; Upper: 7.1
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The American National Standards Institute (ANSI) states that "the odor of toluene is detectable by most people at concentrations in the range of 10 to 15 ppm. The odor has little value as a warning property."

Patty points out that olfactory fatigue occurs rapidly upon exposure to toluene.

2. Eye Irritation Level: Grant states that "the vapors of toluene cause noticeable sensation of irritation to human eyes at 300 to 400 ppm in air, but even at 800 ppm irritation is slight."

ANSI reports that "irritation of eyes, mucous membranes, and upper respiratory tract may occur while workers are exposed to low concentrations of toluene. There is a considerable range of variation (100 to 500 ppm) between individuals, some finding any concentration of toluene objectionable. Commercial grades of toluene vary in irritant properties."

3. Evaluation of Warning Properties: Because of its irritant effects, toluene is judged to have good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of toluene. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of toluene. Each measurement should consist of a 10-minute sample or a series of consecutive samples totalling 10 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent desorption of toluene with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure toluene may be used. An analytical method for toluene is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

Methods for Set V" (order number PB 262 524).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid toluene.
- Any clothing which becomes wet with liquid toluene should be removed immediately and not reworn until the toluene is removed from the clothing.
- Clothing wet with toluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of toluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the toluene, the person performing the operation should be informed of toluene's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid toluene may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to toluene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid toluene should be promptly washed or showered with soap or mild detergent and water to remove any toluene.
- Employees who handle liquid toluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to toluene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in pharmaceutical, chemical, rubber, and plastics industries; as a thinner for paints, lacquer, coatings, and dyes; as a paint remover; insecticides	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as starting material and intermediate in organic chemical and chemical synthesis industries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of artificial leather; fabric and paper coatings; photogravure ink production; spray surface coating; as a diluent (cellulose ester lacquers)	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as constituent in formulation of automotive and aviation fuels	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid toluene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid toluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid toluene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of toluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When toluene has been swallowed, get medical attention immediately. Do not attempt to make the exposed person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If toluene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Toluene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of toluene vapors are permitted.

- Waste disposal method:

Toluene may be disposed of by atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on toluene, look up toluene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Toluene (July 1973)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Toluene*, New York, 1970.

RESPIRATORY PROTECTION FOR TOLUENE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

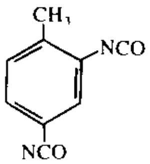
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TOLUENE DIISOCYANATE

INTRODUCTION

This guideline summarizes pertinent information about toluene diisocyanate (TDI) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_9H_6N_2O_2$
- **Structure:**



- **Synonyms:** 2,4-Diisocyanato-1-methyl benzene; TDI; toluene-2, 4-diisocyanate; 2,4-toluene diisocyanate
- **Identifiers:** CAS 584-84-9; RTECS CZ6300000; DOT 2078, label required: "Poison"
- **Appearance and odor:** Colorless to pale yellow liquid with a sharp, pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 174.16
2. Boiling point (at 760 mmHg): 251°C (484°F)
3. Specific gravity (water = 1): 1.22
4. Vapor density (air = 1 at boiling point of TDI): 6.0
5. Melting point: 21°C (69.8°F)
6. Vapor pressure at 25°C (77°F): 0.05 mmHg
7. Insoluble in water (reacts exothermically)
8. Evaporation rate (butyl acetate = 1): Much less than 1
9. Saturation concentration in air (approximate) at 25°C (77°F): 0.00657% (65.7 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with water, acids, bases, and amines may cause reactions that liberate heat and cause violent foaming and spattering.
2. Hazardous decomposition products: Toxic gases and vapors (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving TDI.
3. Caution: TDI will attack some forms of plastic, rubber, and coatings.

- **Flammability**

1. Flash point: 132°C (270°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 0.9; upper, 9.5
3. Extinguishant: Carbon dioxide, dry chemical powder, or foam
4. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

- **Warning properties**

1. Odor threshold: 0.17 ppm
2. Eye irritation levels: 0.05-0.1 ppm
3. Evaluation of warning properties for respirator selection: Because of the lack of odor and irritant effects at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), TDI can only be detected above the NIOSH REL; thus TDI is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TDI is 0.02 parts of TDI per million parts of air (ppm) [0.14 milligrams of TDI per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.005 ppm (0.135 mg/m³) as a time-weighted average (TWA) concentration for up to a 10-hour workshift, 40-hour workweek, and the ceiling concentration is 0.02 ppm (0.14 mg/m³) as determined in any 10-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.005 ppm (0.04 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek, and the short-term exposure limit (STEL) is 0.02 ppm (0.15 mg/m³) (Table 1).

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Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for toluene diisocyanate

	Exposure limits	
	ppm	mg/m³
OSHA PEL ceiling	0.02	0.14
NIOSH REL TWA	0.005	0.035
Ceiling (10 min)	0.02	0.14
ACGIH TLV® TWA	0.005	0.04
STEL	0.02	0.15

HEALTH HAZARD INFORMATION

- **Routes of exposure**

TDI may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Chronic administration of TDI by gavage to rats and mice produced cancer of the skin, pancreas, liver, mammary glands, and blood vessels. Chronic inhalation of TDI by rats caused increased fibrous tissue in the lung bronchioles, inflammation of the lungs and trachea, and death due to hemorrhage in the lungs. NIOSH will continue to monitor the research regarding TDI to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.
2. *Effects on humans:* Exposure to TDI has caused severe bronchospasm, lung inflammation, fluid in the lungs, and decreased breathing capacity. It has also caused sensitization of the respiratory tract, as manifested by acute asthmatic reaction upon return to work after a period of time away from exposure.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to TDI can cause coughing, tightness of the chest, chest pain, nausea, vomiting, abdominal pain, headache, and insomnia. TDI can also cause severe skin irritation with redness, swelling, and blistering, and eye irritation with permanent damage if untreated.
2. *Long-term (chronic):* Exposure to TDI can cause respiratory sensitization; initial symptoms include coughing during the night, with difficult or labored breathing. Skin sensitization can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to TDI, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, eyes, and skin. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to TDI at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. The physician should note that a bronchial challenge test for nonspecific airway hyperreactivity (e.g., to cold air, exercise, methacholine, or histamine) may not be sufficiently sensitive or specific for identifying workers who are susceptible or sensitized to the effects of TDI.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to TDI. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system, eyes, and skin as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, pre- and post-shift tests of lung function, and chest X-rays. At the current state of knowledge, tests for tolyl-specific serum IgE antibodies are not sufficiently sensitive or specific for use in medical screening or diagnosis of bronchial hypersensitivity in workers exposed to TDI.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to TDI may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Extrinsic asthma (acute).
2. Delayed-onset SHE's include: Extrinsic asthma (chronic).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to TDI should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of TDI. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 10-minute sample or a series of consecutive samples that total 10 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting TDI vapors using midget impingers filled with a solution of 1-(2-methoxy phenyl)-piperazine in toluene and analyzing by liquid chromatography with UV detection. Detector tubes or other direct-reading devices calibrated to measure TDI may also be used if available. A detailed sampling and analytical method for TDI may be found in the *NIOSH Manual for Analytical Methods* (method number 2535).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with TDI.

Workers should be provided with and required to use splash-proof safety goggles where TDI may come in contact with the eyes.

SANITATION

Clothing which is contaminated with TDI should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of TDI from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of TDI's hazardous properties. Before being laundered, contaminated clothing shall be placed in a decontaminating solution of water containing 10% ammonia in a container that is impervious to TDI. Caution: Do not tightly close containers used for decontamination because of a possible increase in gas pressure.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with TDI should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle TDI should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to TDI may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for toluene diisocyanate

Operations	Controls
During use in the manufacture of diisocyanatepolyol surface coatings and and finishes, polyurethane paints, and electrical and thermal insulation	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment
During use in the manufacture and curing of flexible polyurethane foams and elastoplastics, adhesives, and sealants	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to TDI, an eye-wash fountain should be provided within the immediate work area for emergency use.

If TDI gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to TDI, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If TDI gets on the skin, wash it immediately with soap and water. If TDI penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If TDI is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing TDI, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from TDI vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing TDI may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. TDI should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing TDI may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**
For each level of respirator protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for toluene diisocyanate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.05 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection) Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 0.125 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1 ppm	Any self-contained breathing apparatus with a full facepiece Any supplied-air respirator with a full facepiece
Less than or equal to 10 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 10 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.005 ppm (0.035 mg/m^3) (TWA) and 0.02 ppm (0.14 mg/m^3) (ceiling).

Occupational Health Guideline for o-Toluidine*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3C_6H_4NH_2$
- Synonyms: Ortho-aminotoluene; o-methylaniline; 1-methyl-2-aminobenzene; 2-methylaniline
- Appearance and odor: Colorless to pale yellow liquid with a weak, aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-toluidine is 5 parts of o-toluidine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 22 milligrams of o-toluidine per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for o-toluidine from 5 ppm to 2 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

o-Toluidine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to o-toluidine may affect the ability of the blood to carry oxygen. The earliest effect from exposure to this chemical is a bluish discoloration of the lips, tongue, and finger nails. At first, if the oxygen lack is not severe, the exposed person may have a feeling of well being. As the lack of oxygen increases, effects such as drowsiness, headache, nausea, and vomiting may appear. If oxygen lack is very severe, it may cause unconsciousness and even death. Liquid toluidine is irritating to the eyes. Recovery from eye exposure may take a long time unless the eyes are flushed with water immediately. In addition, exposure to o-toluidine may cause bloody urine for a short time.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to o-toluidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to o-toluidine at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, kidneys, liver, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: o-Toluidine has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determination should be performed when o-toluidine intoxication is suspected.

- **Summary of toxicology**

o-Toluidine absorption, whether from inhalation of the vapor or by skin absorption of the liquid, causes anoxia (due to the formation of methemoglobin), and hematu-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

ria. The earliest manifestations of poisoning in humans are headache and cyanosis of the lips, the mucous membranes, the fingernail beds, and the tongue. Minor degrees of hypoxia may lead to a temporary sense of well-being and exhilaration. As the lack of oxygen increases, however, there is growing weakness, dizziness, and drowsiness, leading to stupor, unconsciousness, and death if treatment is not prompt. Transient microscopic hematuria has been observed in o-toluidine workers, presumably of renal origin, since no alterations in the bladder mucosa were observed by cystoscopy. In the eye of a rabbit, the liquid caused a severe burn. Excessive drying of the skin may result from repeated or prolonged contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 107
2. Boiling point (760 mm Hg): 199.7 C (391 F)
3. Specific gravity (water = 1): 1.00
4. Vapor density (air = 1 at boiling point of o-toluidine): 3.7
5. Melting point: −16.3 C (−3 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving o-toluidine.
4. Special precautions: Liquid o-toluidine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 85 C (185 F) (closed cup)
2. Autoignition temperature: 482 C (900 F)
3. Flammable limits in air, % by volume: Lower: 1.5 (calculated at flash point)
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The Manufacturing Chemists Association reports that o-toluidine has an aromatic, aniline-like odor, but no information is available concerning the odor threshold of this substance. Aniline, o-toluidine, and xylidine, however, represent a family of chemical compounds with increasing methyl substitution. Since aniline has an odor threshold of 7 ppm and xylidine has an odor threshold of 0.0048 ppm, it is reasonable to assume that the aniline-like odor of o-toluidine is detectable at a concentration between 0.0048 and 7 ppm.
2. Eye Irritation Level: o-Toluidine vapor is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of o-toluidine is probably near the TLV, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of o-toluidine in an adsorption tube containing silica gel, followed by desorption with ethanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure o-toluidine may be used. An analytical method for o-toluidine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid o-toluidine.
- Clothing contaminated with o-toluidine should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of o-toluidine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-toluidine, the person performing the operation should be informed of o-toluidine's hazardous properties.

- Where exposure of an employee's body to liquid o-toluidine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with o-toluidine should be removed immediately and not reworn until the o-toluidine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of liquid o-toluidine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid o-toluidine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with o-toluidine should be immediately washed or showered with soap or mild detergent and water to remove any o-toluidine.
- Eating and smoking should not be permitted in areas where liquid o-toluidine is handled, processed, or stored.
- Employees who handle liquid o-toluidine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to o-toluidine may occur and control methods which may be effective in each case:

Operation	Controls
Use in dye industry in manufacture of dyes and dye intermediates; use in chemical industry in manufacture of organic chemicals and chemical intermediates	Process enclosure; general dilution ventilation; personal protective equipment
Use as a reagent chemical in blood sugar determinations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid o-toluidine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid o-toluidine gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid o-toluidine soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of o-toluidine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid o-toluidine has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the person to vomit by having him touch the back of his throat with his finger or by giving him large amounts of warm water. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If o-toluidine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

o-Toluidine may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

o-Toluidine appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 16, 1978.

RESPIRATORY PROTECTION FOR o-TOLUIDINE

Condition	**Minimum Respiratory Protection* Required Above 5 ppm**
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Tributyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_4H_9O)_3PO$
- Synonyms: Tri-n-butyl phosphate; TBP
- Appearance and odor: Colorless to pale yellow, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tributyl phosphate is 5 milligrams of tributyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for tributyl phosphate from 5 mg/m^3 to 2.5 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tributyl phosphate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Tributyl phosphate may cause irritation of the eyes, nose, and throat. It may also cause nausea and headache.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tributyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tributyl phosphate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from tributyl phosphate exposure.

—Chronic respiratory disease: Tributyl phosphate causes respiratory irritation. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of tributyl phosphate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Tributyl phosphate is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Tributyl phosphate vapor is a pulmonary irritant and, in animals, causes a moderate excitation of the nervous system. In rats, the oral LD50 is 3 g/kg; the effects are muscle twitching, weakness, dyspnea, and pulmonary edema. In vitro, tributyl phosphate causes weak inhibition of cholinesterases in human erythrocytes and plasma. Workers exposed to unspecified concentrations of vapor complained of headache and nausea; hot vapor was severely irritating to the eyes and throat. The liquid dropped on the eye of a rabbit caused temporary epithelial injury and discomfort. The liquid may be irritating to the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 266
2. Boiling point (760 mm Hg): 293 C (560 F)
3. Specific gravity (water = 1): 0.97
4. Vapor density (air = 1 at boiling point of tributyl phosphate): Not applicable

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National Institute for Occupational Safety and Health

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Occupational Safety and Health Administration

5. Melting point: Less than −80 C (−112 F)

6. Vapor pressure at 20 C (68 F): Very low

7. Solubility in water, g/100 g water at 20 C (68 F): 0.1

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: None

3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving tributyl phosphate.

4. Special precautions: Liquid tributyl phosphate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 166 C (330 F) (closed cup)

2. Autoignition temperature: Higher than 482 C (900 F)

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of tributyl phosphate.

2. Eye Irritation Level: Grant states that tributyl phosphate, "tested on rabbit eyes by application of a drop, . . . had an effect similar to ethyl alcohol, causing temporary epithelial injury and pain, a reaction graded 3 on a scale of 1 to 10 after 24 hours, but no permanent injury." According to the *Hygienic Guide*, some eye irritation occurs at vapor concentrations of ethyl alcohol which are greater than 5500 ppm. Tributyl phosphate and ethyl alcohol in liquid form produce similar effects on the eye.

3. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of tributyl phosphate to air concentrations, this substance is treated as having poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of tributyl phosphate on a filter, followed by extraction with ether, and gas chromatographic analysis. An analytical method for tributyl phosphate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid tributyl phosphate.
- Clothing wet with liquid tributyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tributyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tributyl phosphate, the person performing the operation should be informed of tributyl phosphate's hazardous properties.
- Non-impervious clothing which becomes wet with liquid tributyl phosphate should be removed promptly and not reworn until the tributyl phosphate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid tributyl phosphate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid tributyl phosphate should be promptly washed or showered with soap or mild detergent and water to remove any tributyl phosphate.
- Employees who handle liquid tributyl phosphate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tributyl phosphate may occur and control methods which may be effective in each case:

Operation	Controls
Use as an antifoaming agent or plasticizer in manufacture of surface coatings and adhesives for latex exterior paints, pigment coatings for paper, inks, lacquers, and synthetic enamel finishes, and during milling pigments	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent in extraction of metals, including uranium, tharium, and rare earths in atomic energy processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a heat-exchange medium in aircraft engines	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid tributyl phosphate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid tributyl phosphate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid tributyl phosphate soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of tributyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid tributyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid tributyl phosphate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Liquid tributyl phosphate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Tributyl Phosphate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR TRIBUTYL PHOSPHATE

Condition	**Minimum Respiratory Protection*** **Required Above 5 mg/m³**
Particulate or Vapor Concentration	
50 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m³ or less	A gas mask with a chin-style or a front- or back-mounted organic vapor cartridge and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1300 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1300 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,1,2-Trichloroethane *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CHCl_2CH_2Cl$
- Synonyms: Vinyl trichloride; beta-trichloroethane
- Appearance and odor: Colorless liquid with a sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2-trichloroethane is 10 parts of 1,1,2-trichloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 45 milligrams of 1,1,2-trichloroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2-Trichloroethane can affect the body if it is inhaled if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: 1,1,2-Trichloroethane may cause irritation of the eyes and nose, drowsiness, incoordination, unconsciousness, and death. It might also cause liver and kidney damage.

2. Long-term Exposure: Repeated or prolonged exposure to 1,1,2-trichloroethane might cause liver or kidney damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2-trichloroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1,2-trichloroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1,2-trichloroethane exposure.

—Liver disease: 1,1,2-Trichloroethane causes liver damage in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: 1,1,2-Trichloroethane causes kidney damage in animals and justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,1,2-Trichloroethane vapor is a potent narcotic. Injury to lungs, liver, and kidneys has been observed in animals. The lethal concentration for rats was 2000 ppm for 4 hours. Concentrations resulting in narcosis also caused irritation of the nose and eyes. Mice treated by intraperitoneal injection with anesthetic doses showed moderate hepatic dysfunction and renal dysfunction; at autopsy, there was centrolobular necrosis of the liver and tubular necrosis of the kidney. No human cases of intoxication or systemic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 133.4
2. Boiling point (760 mm Hg): 113 C (236 F)
3. Specific gravity (water = 1): 1.43
4. Vapor density (air = 1 at boiling point of 1,1,2-trichloroethane): 4.55
5. Melting point: −37 C (−34 F)
6. Vapor pressure at 20 C (68 F): 18.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F):

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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0.45

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as aluminum and magnesium powders, sodium or potassium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,1,2-trichloroethane.
4. Special precautions: Liquid 1,1,2-trichloroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: None in normal test method
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 6.0; Upper: 15.5 (high energy ignition source required)
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Although 1,1,2-trichloroethane is known to have a sweet, chloroform-like odor, no quantitative data are available concerning the odor threshold of this substance.
2. Eye Irritation Level: Grant reports that high concentrations of the vapors are irritating to the eyes. The concentrations at which this irritation occurs are not stated.
3. Other Information: Grant reports that high concentrations of the vapors are irritating to the respiratory tract, but no quantitative information is given.
4. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties to air concentrations of 1,1,2-trichloroethane, this substance has been treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,2-trichloroethane may be used. An analytical method for 1,1,2-trichloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1,2-trichloroethane.
- Clothing wet with liquid 1,1,2-trichloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1,2-trichloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1,2-trichloroethane, the person performing the operation should be informed of 1,1,2-trichloroethane's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid 1,1,2-trichloroethane should be removed promptly and not reworn until the 1,1,2-trichloroethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1,2-trichloroethane may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid 1,1,2-trichloroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1,2-trichloroethane.

- Eating and smoking should not be permitted in areas where liquid 1,1,2-trichloroethane is handled, processed, or stored.
- Employees who handle liquid 1,1,2-trichloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2-trichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in organic synthesis in production of vinylidene chloride	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,1,2-trichloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1,2-trichloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2-trichloroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1,2-trichloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1,2-trichloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1,2-trichloroethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, or a similar material.

- Waste disposal method:

1,1,2-Trichloroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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* SPECIAL NOTE

1,1,2-Trichloroethane appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR 1,1,2-TRICHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TRICHLOROETHYLENE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about trichloroethylene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2HCl_3
- **Structure:** $CCl_2 = CHCl$
- **Synonyms:** Acetylene trichloride, ethylene trichloride, TCE
- **Identifiers:** CAS 79-01-6; RTECS KX455000; DOT 1710, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless liquid with a sweet odor like chloroform

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 131.38
2. Boiling point (at 760 mmHg): 87.1°C (188°F)
3. Specific gravity (water = 1): 1.46
4. Vapor density (air = 1 at boiling point of trichloroethylene): 4.54
5. Melting point: -86.4°C (-123°F)
6. Vapor pressure at 25°C (77°F): 74.3 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 0.00011
8. Evaporation rate (butyl acetate = 1): 6.2
9. Saturation concentration in air (approximate) at 25°C (77°F): 10.1% (101,000 ppm)
10. Ionization potential: 9.47 eV

- **Reactivity**

1. Incompatibilities: Trichloroethylene may react violently with chemically active metals such as barium, lithium, sodium, magnesium, and titanium. Aluminum may react with the free hydrogen chloride in trichloroethylene to produce aluminum chloride, which catalyzes a violent self-accelerating polymerization reaction. Contact with strong caustics may cause the formation of dichloracetylene, a toxic and flammable gas.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving trichloroethylene.

- **Flammability**

1. Flash point: 32°C (90°F) (closed cup)
2. Autoignition temperature: 788°C (420°F)
3. Flammable limits in air, % by volume: Lower, 12.5; Upper, 90
4. Extinguishant: Alcohol foam, dry chemical, or carbon dioxide
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 1, Practically Nonflammable (NFPA)

- **Warning properties**

1. Odor threshold: 21.4 ppm
2. Eye irritation level: 400 ppm
3. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for trichloroethylene per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 200 ppm; and the maximum peak concentration above the acceptable ceiling (maximum duration of 5 minutes in any 2-hour period) is 300 ppm. The National Institute for Occupational Safety and Health (NIOSH) recommends that trichloroethylene be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (270 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 200 ppm (1,080 mg/m³) (Table 1).

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Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for trichloroethylene

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	100	—
Acceptable ceiling	200	—
Maximum ceiling (5 min in 2 h)	300	—
NIOSH REL TWA (Ca)*	25	—
ACGIH TLV® TWA	50	270
STEL	200	1,080

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trichloroethylene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of trichloroethylene by multiple species of animals caused depressed brain function, brain damage, liver and kidney injury, and death due to respiratory failure or cardiac arrest. In rats, rabbits, guinea pigs, and gerbils, chronic inhalation of trichloroethylene caused toxic effects on the nerves, increases in liver and kidney weights, and suppression of growth. Chronic oral administration of trichloroethylene to mice produced cancers of the liver and lungs, and chronic inhalation by female mice produced cancers of the lymph system and lungs.

2. *Effects on humans:* Acute inhalation or ingestion of trichloroethylene has caused reversible peripheral nerve degeneration, injury to the liver and kidneys and to the cardiovascular and gastrointestinal systems, depression of the central nervous system, coma, and sudden death due to respiratory failure, cardiac arrhythmia, or liver or kidney failure. Chronic exposure to trichloroethylene has caused damage to the liver, kidneys, and nervous system. The ingestion of alcohol, caffeine, and some prescription drugs has been found to potentiate the effects of trichloroethylene intoxication. A dermal response seen as a reddening of the face, neck, back, and shoulders (degreaser's flush) has occurred in chronically exposed workers following the ingestion of alcohol. Repeated immersion of the hands into liquid trichloroethylene has caused paralysis of the fingers.

- **Signs and symptoms of exposure**

1. *Short-term (acute):* Inhalation exposure to trichloroethylene can cause drowsiness, dizziness, headache, blurred vision, incoordination, mental confusion, flushed skin, tremors, nausea, vomiting, fatigue, and cardiac arrhythmia. Irritation of the skin, mucous membranes, and eyes can also occur.

2. *Long-term (chronic):* Exposure can cause headache, cough, double vision, impaired coordination and senses of touch and smell, anxiety, dizziness, giddiness, weakness, tremor, slowness of heartbeat, and intolerance to alcohol. Dryness of the skin, blisters, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

- **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, and morbidity and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

- **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to trichloroethylene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and cardiovascular, nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to trichloroethylene at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the skin or liver. The physician should obtain baseline values for liver function tests.

- **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to trichloroethylene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the eyes, skin, liver, kidneys, and cardiovascular, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to trichloroethylene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to trichloroethylene should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting trichloroethylene vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure trichloroethylene may also be used if available. A detailed sampling and analytical method for trichloroethylene may be found in the *NIOSH Manual of Analytical Methods* (method number S336).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with trichloroethylene.

SANITATION

Clothing which is contaminated with trichloroethylene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of trichloroethylene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of trichloroethylene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with trichloroethylene should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle trichloroethylene should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to trichloroethylene may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for trichloroethylene

Operations	Controls
During use as a cleaning solvent in cold cleaning and vapor degreasing operations	Process enclosure, local exhaust ventilation, personal protective equiment
During use as a scouring and cleaning agent in textile processing; during use in the extraction and purification of animal and vegetable oils in food and pharmaceutical industries; during use in chemical synthesis	Process enclosure, local exhaust ventilation
During use in the manufacture of adhesives, anesthetics and analgesics, and cleaning and polishing preparations	Process enclosure, local exhaust ventilation
During use as a fumigant and disintectant for seeds and grains	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to trichloroethylene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If trichloroethylene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to trichloroethylene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If trichloroethylene gets on the skin, wash it immediately with soap and water. If trichloroethylene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If trichloroethylene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing trichloroethylene, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing trichloroethylene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. Liquids containing trichloroethylene may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for trichloroethylene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Trichloronaphthalene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_5Cl_3$
- Synonyms: Halowax; Seekay wax; nibren wax
- Appearance and odor: Colorless to pale yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for trichloronaphthalene is 5 milligrams of trichloronaphthalene per cubic meter of air (mg/m³) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trichloronaphthalene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

Exposure to trichloronaphthalene may cause an acne-like rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to trichloronaphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to trichloronaphthalene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and skin should be stressed.

—Liver function tests: Trichloronaphthalene may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Trichloronaphthalene vapor and dust are toxic to the liver and the skin. Rats exposed to a mixture of tri- and tetrachloronaphthalene at 11 mg/m³, 16 hours daily for 2-½ months showed slightly swollen liver cells with granular cytoplasm. An industrial exposure to unknown concentrations caused a severe acne-form dermatitis (chloracne) in 50 workers (89% of the crew); initially there was pruritis, which progressed to an acute eczema and finally a subacute folliculitis of acne type affecting mainly the face, periorbital region, cheeks, and ears. Two workers experienced anorexia, nausea, and vertigo. No fatal cases of liver injury have been reported, but one instance of toxic hepatitis resulted from exposure to 3 mg/m³.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 231.4
2. Boiling point (760 mm Hg): 304— 354 C (580—670 F)
3. Specific gravity (water = 1): 1.58
4. Vapor density (air = 1 at boiling point of trichloronaphthalene): 8.0
5. Melting point: 93 C (199 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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8. Evaporation rate (butyl acetate = 1): Much less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving trichloronaphthalene.
4. Special precautions: None known.

- **Flammability**

1. Flash point: 200 C (392 F) (open cup)
2. Autoignition temperature: None to boiling point
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Since there are no quantitative data relating warning properties to air concentrations of trichloronaphthalene, this substance is treated as a material with poor warning properties. The concentration of trichloronaphthalene in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

Even though the AIHA *Hygienic Guide* states that "eye injury has not proved to be troublesome with the chloronaphthalenes," trichloronaphthalene is treated as an eye irritant for the purposes of this guideline, as a Koppers Corporation *Material Safety Data Sheet* states that the vapors or dust may irritate the eyes.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of trichloronaphthalene on a filter and in a bubbler containing iso-octane, followed by extraction with iso-octane, and gas chromatographic analysis. An analytical method for trichloronaphthalene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with molten trichloronaphthalene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid trichloronaphthalene or liquids containing trichloronaphthalene.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with trichloronaphthalene fumes from the heated material.
- Non-impervious clothing which becomes contaminated with molten trichloronaphthalene should be removed immediately and not reworn until the trichloronaphthalene is removed from the clothing.
- Non-impervious clothing which becomes contaminated with solid trichloronaphthalene or liquids containing trichloronaphthalene should be removed promptly and not reworn until the trichloronaphthalene is removed from the clothing.
- If employees' clothing may have become contaminated with solid trichloronaphthalene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with trichloronaphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of trichloronaphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to

remove the trichloronaphthalene, the person performing the operation should be informed of trichloronaphthalene's hazardous properties.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten trichloronaphthalene contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid trichloronaphthalene or liquids containing trichloronaphthalene may contact the eyes.

SANITATION

- Workers subject to skin contact with trichloronaphthalene should wash with soap or mild detergent and water any areas of the body which may have contacted trichloronaphthalene at the end of each work day.
- Skin that becomes contaminated with trichloronaphthalene should be promptly washed or showered with soap or mild detergent and water to remove any trichloronaphthalene.
- Employees who handle trichloronaphthalene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to trichloronaphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Use as an insulating material in pouring, dipping, and covering of electrical equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of electrical equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an inert component for resins or polymers as a flame-resistant, water-proofing, and fungicidal/insecticidal agent in coatings for wood, textiles, and paper	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in catalytic chlorination of naphthalene to produce tetrachloronaphthalene and trichloronaphthalene; as a filler to impart flame resistance and improve electrical resistance to polymers; manufacture of special lubricants	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive for cutting oil	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive to special lubricants in crankcase oil, lubricants for farm machinery, and as an extreme-pressure lubricant	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid trichloronaphthalene or liquids containing trichloronaphthalene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. If molten trichloronaphthalene gets into the eyes, immediately flush the eyes with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If solid trichloronaphthalene or liquids containing trichloronaphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If trichloronaphthalene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention. If molten trichloronaphthalene gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of trichloronaphthalene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When trichloronaphthalene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If trichloronaphthalene is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other flammable material, place in an appropriate container and burn in a safe place (such as a fume hood.) Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Trichloronaphthalene may be disposed of:

1. By making packages of trichloronaphthalene in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR TRICHLORONAPHTHALENE

Condition	**Minimum Respiratory Protection*** **Required Above 5 mg/m³**
Particulate Concentration	
50 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for 1,2,3-Trichloropropane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_2ClCHClCH_2Cl$
- Synonyms: Allyl trichloride; glycerol trichlorohydrin; glycerin trichlorohydrin; trichlorohydrin
- Appearance and odor: Colorless liquid with a strong acid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,2,3-trichloropropane is 50 parts of 1,2,3-trichloropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of 1,2,3-trichloropropane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,2,3-Trichloropropane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: 1,2,3-Trichloropropane may cause irritation of the eyes, nose, and throat. It might cause drowsiness and liver damage.

2. Long-term Exposure: 1,2,3-Trichloropropane might cause irritation from prolonged or repeated exposure.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,2,3-trichloropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,2,3-trichloropropane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,2,3-trichloropropane exposure.

—Skin disease: 1,2,3-Trichloropropane is a skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: 1,2,3-Trichloropropane is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although 1,2,3-trichloropropane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,2,3-trichloropropane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,2,3-Trichloropropane vapor is a narcotic, irritates the upper respiratory tract, and is toxic to the liver. Inhalation by mice of 30 mg/liter (5,000 ppm) for 20 minutes was fatal to 8 of 15 exposed; liver damage accounted for four additional deaths 7 to 10 days later; daily 10-minute exposures at 2,500 ppm for 10 days resulted in 7 deaths among 10 mice. In rabbits the liquid was an intense skin irritant and caused erythema, sloughing, and cracking. In an experimental human study, exposure to 100 ppm

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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was objectionable because of eye and throat irritation and unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 147.4
2. Boiling point (760 mm Hg): 156 C (313 F)
3. Specific gravity (water = 1): 1.4
4. Vapor density (air = 1 at boiling point of 1,2,3-trichloropropane): 5
5. Melting point: −14.7 C (5 F)
6. Vapor pressure at 20 C (68 F): 3.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with active metals, strong caustics, or with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,2,3-trichloropropane.
4. Special precautions: 1,2,3-Trichloropropane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 73.3 C (164 F) (closed cup)
2. Autoignition temperature: 304 C (579 F)
3. Flammable limits in air, % by volume: Lower: 3.2%; Upper: 12.6%
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

The *Documentation of TLV's* reports that "the vapor of 1,2,3-trichloropropane was objectionable to all subjects exposed at a concentration of 100 ppm because of eye irritation, throat irritation, and unpleasant odor." Since this concentration is only twice the permissible exposure limit, this compound is considered to have adequate warning properties.

As mentioned above, the *Documentation of TLV's* states that 100 ppm causes eye irritation. However, this is not reported as a threshold level.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,2,3-trichloropropane may be used. An analytical method for 1,2,3-trichloropropane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,2,3-trichloropropane.
- Clothing contaminated with liquid 1,2,3-trichloropropane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,2,3-trichloropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,2,3-trichloropropane, the person performing the operation should be informed of 1,2,3-trichloropropane's hazardous properties.
- Where exposure of an employee's body to liquid 1,2,3-trichloropropane may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid 1,2,3-trichloropropane should be re-

moved immediately and not reworn until the 1,2,3-trichloropropane is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid 1,2,3-trichloropropane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid 1,2,3-trichloropropane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid 1,2,3-trichloropropane should be immediately washed or showered with soap or mild detergent and water to remove any 1,2,3-trichloropropane.
- Eating and smoking should not be permitted in areas where liquid 1,2,3-trichloropropane is handled, processed, or stored.
- Employees who handle liquid 1,2,3-trichloropropane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,2,3-trichloropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent and extractant for resins, oils, fats, waxes, and chlorinated rubber; as a commercial solvent for degreasing metal parts	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for the manufacture of other chemicals; use as a copolymer or telomer or cross-linking agent for sealing compounds	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,2,3-trichloropropane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,2,3-trichloropropane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,2,3-trichloropropane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,2,3-trichloropropane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,2,3-trichloropropane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,2,3-trichloropropane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

1,2,3-Trichloropropane may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "1,2,3-Trichloropropane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR 1,2,3-TRICHLOROPROPANE

Condition	**Minimum Respiratory Protection* Required Above 50 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

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*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of 1,2,3-trichloropropane; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 1000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for 1,1,2-Trichloro-1,2,2-Trifluoroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CCl_2F\text{-}CClF_2$
- Synonyms: Halocarbon 113; Refrigerant 113; TTE
- Appearance and odor: Colorless liquid with an odor like carbon tetrachloride (at high concentrations).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2-trichloro-1,2,2-trifluoroethane is 1000 parts of 1,1,2-trichloro-1,2,2-trifluoroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7600 milligrams of 1,1,2-trichloro-1,2,2-trifluoroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2-Trichloro-1,2,2-trifluoroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: 1,1,2-Trichloro-1,2,2-trifluoroethane may cause irritation of the eyes and throat or drowsiness. Breathing high concentrations may cause the heart to beat irregularly or to stop.

2. Long-term Exposure: 1,1,2-Trichloro-1,2,2-trifluoroethane on prolonged or repeated contact with the skin may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2-trichloro-1,2,2-trifluoroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1,2-trichloro-1,2,2-trifluoroethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1,2-trichloro-1,2,2-trifluoroethane exposure.

—Skin disease: 1,1,2-Trichloro-1,2,2-trifluoroethane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrythmias, the breathing of 1,1,2-trichloro-1,2,2-trifluoroethane might cause exacerbation of symptoms due to its sensitizing properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1,1,2-Trichloro-1,2,2-trifluoroethane vapor is a narcotic. In guinea pigs exposed to 25,000 ppm, nasal irritation was rapidly apparent and incoordination occurred at 50,000 ppm after 30 minutes; death occurred after one hour at this level. In dogs, cardiac sensitization to epinephrine occurred at concentrations of 5,000 to 10,000 ppm. The liquid produced no irritation on the abraded or intact skin of guinea pigs; in the eyes of rabbits it produced mild conjunctivitis and minimal corneal dullness, which were reversible. In experimental human studies, exposure to 4,500 ppm for 30 to 100 minutes resulted in significant impairment in tests of manual dexterity and vigilance; subjects reported loss of concentration and a tendency to somnolence which disappeared 15 minutes after the exposure ended; at

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1,500 ppm no effects were observed. More prolonged human exposures of 6 hours daily, 5 days per week for 2 weeks at concentrations of approximately 500 and 1,000 ppm resulted in no adverse effects, with the exception of mild throat irritation on the first day; there was no decrement in performance of complex mental tasks. The liquid dissolves the natural oils of the skin, and dermatitis may occur as a result of repeated contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 187.4
2. Boiling point (760 mm Hg): 47.6 C (117.6 F)
3. Specific gravity (water = 1): 1.55
4. Vapor density (air = 1 at boiling point of 1,1,2-trichloro-1,2,2-trifluoroethane): 6.5
5. Melting point: −35 C (−31 F)
6. Vapor pressure at 20 C (68 F): 284 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.017
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Reacts with chemically active metals such as calcium, powdered aluminum, zinc, magnesium and beryllium. Contact with magnesium alloys containing more than 2% magnesium may cause decomposition.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, hydrogen fluoride, phosgene, and carbon monoxide) may be released when 1,1,2-trichloro-1,2,2-trifluoroethane decomposes.
4. Special precautions: 1,1,2-Trichloro-1,2,2-trifluoroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Since the AIHA *Hygienic Guide* states that this compound is "nearly odorless," and since experimental evidence indicates that its irritant effects are only slight and transient at concentrations near the permissible exposure, it is treated as a material with poor warning properties.

There is no evidence to indicate that the vapor is an eye irritant. The *Documentation of TLV's* states that "no corneal injury or irritation" was observed in guinea pigs exposed to this substance. For the purposes of this guideline, therefore, it is not treated as an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,2-trichloro-1,2,2-trifluoroethane may be used. An analytical method for 1,1,2-trichloro-1,2,2-trifluoroethane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).
(order number PB 265 028).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1,2-trichloro-1,2,2-trifluoroethane.
- Non-impervious clothing which becomes wet with liquid 1,1,2-trichloro-1,2,2-trifluoroethane should be removed promptly and not reworn until the 1,1,2-trichloro-1,2,2-trifluoroethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid 1,1,2-trichloro-1,2,2-trifluoroethane contacting the eyes.

SANITATION

- Skin that becomes wet with liquid 1,1,2-trichloro-1,2,2-trifluoroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1,2-trichloro-1,2,2-trifluoroethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2-trichloro-1,2,2-trifluoroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a selective solvent in degreasing electrical equipment, photographic films, magnetic tapes, precision instruments, plastics, glass, elastomers, or metal components; as dry cleaning solvent for all fabrics, leather, and suedes.	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a refrigerant in commercial/industrial air conditioning and industrial process cooling	General dilution ventilation
Use as a chemical intermediate for dechloronization of chemicals in the manufacture of polymers, and copolymers in production of high-temperature lubricants	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a foaming or blowing agent in the manufacture of polymers for flame retardancy	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a solvent in the textile industry; and as a solvent in special laboratory usage	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If 1,1,2-trichloro-1,2,2-trifluoroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1,2-trichloro-1,2,2-trifluoroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2-trichloro-1,2,2-trifluoroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1,2-trichloro-1,2,2-trifluoroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1,2-trichloro-1,2,2-trifluoroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1,2-trichloro-1,2,2-trifluoroethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

1,1,2-Trichloro-1,2,2-trifluoroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "1,1,2-Trichloro-1,2,2-Trifluoroethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "1,1,2-Trichloro-1,2,2-Trifluoroethane," *Hygienic Guide Series*, Detroit, Michigan, 1968.
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RESPIRATORY PROTECTION FOR 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Vapor Concentration	
4500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 4500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Trifluoromonobromomethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CBrF_3$
- Synonyms: Halocarbon 13B1; Refrigerant 13B1; bromotrifluoromethane; Halon 1301
- Appearance and odor: Colorless gas with a slight ethereal odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for trifluoromonobromomethane is 1000 parts of trifluoromonobromomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6100 milligrams of trifluoromonobromomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trifluoromonobromomethane can affect the body if it is inhaled. It may also affect the body if the liquid comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Breathing high concentrations of trifluoromonobromomethane may cause lightheadedness. Breathing very high concentrations of trifluoromonobromomethane may cause the heart to beat irregularly or stop.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to trifluoromonobromomethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to trifluoromonobromomethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from trifluoromonobromomethane exposure.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrythmias, the breathing of trifluoromonobromomethane might cause exacerbation of symptoms due to its sensitizing properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Trifluoromonobromomethane vapor is a narcotic at high concentrations. In dogs and rats repeatedly exposed to 23,000 ppm there were no toxic signs or pathologic changes. Monkeys exposed to concentrations of 20% (200,000 ppm) became lethargic and suffered spontaneous cardiac arrhythmias within 5 to 40 seconds of exposure. In animal exposure studies at high levels, sensitization of the myocardium to epinephrine was reported. In human experiments designed to determine the safety of the substance as a firefighting agent in airplane cabins, exposure of three volunteers at 7% (70,000 ppm) for three minutes produced no cardiac anomalies.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 149
  2. Boiling point (760 mm Hg): −57.8 C (−72 F)
  3. Specific gravity (water = 1): 1.54 at 77 F

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4. Vapor density (air = 1 at boiling point of trifluoromonobromomethane): 5

5. Melting point: −168 C (−270 F)

6. Vapor pressure at 20 C (68 F): Not pertinent

7. Solubility in water, g/100 g water at 20 C (68 F): 0.03

8. Evaporation rate (butyl acetate = 1): Not pertinent

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Reacts with chemically active metals, calcium, or with powdered aluminum, zinc, and magnesium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, carbonyl fluoride, hydrogen fluoride, and carbon monoxide) may be released when trifluoromonobromomethane decomposes.

4. Special precautions: Liquid trifluoromonobromomethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Trifluoromonobromomethane does not have adequate warning properties.

Trifluoromonobromomethane is not a known eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with methylene chloride and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure trifluoromonobromomethane may be used. An analytical method for trifluoromonobromomethane is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to trifluoromonobromomethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as commercial and military fire extinguishant; use as a refrigerant for food processing and storage; use as a blowing agent to improve flame retardancy of rigid polyurethane foams	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in production of olefin resins; use during the manufacture of hydraulic fluids as an erosion inhibitor	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during use for special purposes in bubble chambers for ionization studies, in "quark" detection, and in radiation counters	General dilution ventilation; local exhaust ventilation; perosnal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of trifluoromonobromomethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If trifluoromonobromomethane is leaked, the following steps should be taken:

1. Ventilate area of leak.
2. Stop flow of gas.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Trifluoromonobromomethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- E. I. DuPont de Nemours and Company: *Freon Compounds and Safety – Trifluoromonobromomethane*, Wilmington, Delaware.
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- National Academy of Sciences: "Symposium on An Appraisal of Halogenated Fire Extinguishing Agents," Washington, D. C., April 11-12, 1972.
- Smith, D. G., and Harris, D. J.: "Human Exposure to Halon 1301 (CBrF3) during Simulated Aircraft Cabin Fires," *Aerospace Medicine*, 44:198-201, 1973.
- Van Stee, E. W., and Back, K. C.: "Short Term Inhalation of Bromotrifluoromethane," *Toxicology and Applied Pharmacology*, 15:164-174, 1969.

RESPIRATORY PROTECTION FOR TRIFLUOROMONOBROMOMETHANE

Condition	**Minimum Respiratory Protection* Required Above 1000 ppm**
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator with a half-facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 50,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Triethylamine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5)_3N$
- Synonyms: None
- Appearance and odor: Colorless liquid with a fishy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for triethylamine is 25 parts of triethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of triethylamine per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Triethylamine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Triethylamine causes irritation of the eyes, nose, and throat. If the liquid is splashed in the eyes, it may cause severe eye damage.

2. Long-term Exposure: Repeated or prolonged exposure to triethylamine may cause skin and lung irritation. Heart, liver, and kidney damage have been reported in animal experiments.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to triethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to triethylamine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from triethylamine exposure.

—Chronic respiratory disease: Triethylamine causes lung irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of triethylamine might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: Triethylamine causes myocardial degeneration in animals. In persons with impaired cardiovascular function, the inhalation of triethylamine might cause exacerbation of pre-existing disorders.

—Liver disease: Triethylamine causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Triethylamine causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Eye disease: Triethylamine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Triethylamine vapor is a primary irritant of mucous membranes and eyes. Exposure to 1000 ppm for 4 hours was lethal to rats. Rabbits survived exposures to 100 ppm daily for 6 weeks, but showed pulmonary irritation, myocardial degeneration, and cellular necrosis of

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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liver and kidney; at 50 ppm the effects on lung, liver, and kidney were less severe, but there was also damage to the cornea. In the eye of a rabbit, 1 drop of liquid triethylamine caused severe injury. Eye irritation and corneal edema in humans have been reported from industrial exposure. Closely related amines cause skin irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 101.2
2. Boiling point (760 mm Hg): 89.5 C (193 F)
3. Specific gravity (water = 1): 0.73
4. Vapor density (air = 1 at boiling point of triethylamine): 3.5
5. Melting point: −115 C (−175 F)
6. Vapor pressure at 20 C (68 F): 54 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 5.5
8. Evaporation rate (butyl acetate = 1): 5.6

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause violent spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving triethylamine.
4. Special precautions: Liquid triethylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −6.7 C (20 F) (closed cup)
2. Autoignition temperature: 450 C (842 F)
3. Flammable limits in air, % by volume: Lower: 1.2; Upper: 8.0
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Grant reports that triethylamine has a "strong ammoniacal odor," but no quantitative information concerning the odor threshold is available.
2. Eye Irritation Level: Grant reports that "chronic exposure of rabbits to triethylamine vapors at concentrations as low as 50 ppm in air causes multiple erosions of the cornea and conjunctiva . . . in the course of 6 weeks."
3. Other Information: Patty reports that rabbits repeatedly exposed to 50 ppm triethylamine over a 6-week period experienced lung irritation.
4. Evaluation of Warning Properties: Since information concerning the odor threshold is not available, and since the only quantitative information concerning its irritant effects is from chronic exposures, triethylamine is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of triethylamine in a bubbler containing sulfuric acid, followed by treatment with sodium hydroxide, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure triethylamine may be used. An analytical method for triethylamine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid triethylamine.
- Clothing wet with liquid triethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

triethylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the triethylamine, the person performing the operation should be informed of triethylamine's hazardous properties.

- Where exposure of an employee's body to liquid triethylamine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with triethylamine or non-impervious clothing which becomes contaminated with triethylamine should be removed immediately and not reworn until the triethylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid triethylamine or liquids containing triethylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid triethylamine or liquids containing 1% or more of triethylamine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with triethylamine should be immediately washed or showered to remove any triethylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to triethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in polymer technology as a catalyst for curing epoxy resins, for polyurethane foams, and for thermosetting polymers; as a stabilizing agent and chain-transfer agent; use in preparation of film-forming resins, as a solvent, pH stabilizer, and to improve water solubility in polymers	Local exhaust ventilation; general dilution ventilation
Use in extraction and purification of antibiotics; use in herbicides and pesticides, and in preparation of emulsifiers for pesticides	Local exhaust ventilation; general dilution ventilation
Use in organic synthesis of quarternary ammonium compounds in textile-treating chemicals, emulsifiers, surfactants, in paper manufacture, non-nutritive sweeteners, ketenes, and salts	Local exhaust ventilation; general dilution ventilation
Use as a corrosion inhibitor and chemical stabilizer for chlorinated solvents, in transmission fluids, oil well piping, engine parts, and gum inhibitors for gasoline	Local exhaust ventilation; general dilution ventilation
Use in paints and coatings to control viscosity and to prevent livering; to develop water resistance in resins; as a pH stabilizer; and to improve gloss of appliance finishes	Local exhaust ventilation; general dilution ventilation
Use as a dye assist; miscellaneous uses in rocket fuels to shorten ignition delays; ingredient of photographic development accelerator, for drying of printing inks, and in carpet cleaners	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If triethylamine or liquids containing triethylamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If triethylamine gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If triethylamine soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of triethylamine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When triethylamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If triethylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Triethylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Triethylamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Triethylamine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.
- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Triethylamine*, New York, 1970.

RESPIRATORY PROTECTION FOR TRIETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against triethylamine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Trinitrotoluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3C_6H_2(NO_2)_3$
- Synonyms: TNT; trinitrotoluol; 2,4,6-trinitrotoluene; sym-trinitrotoluene
- Appearance and odor: Colorless to pale yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for trinitrotoluene is 1.5 milligrams of trinitrotoluene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for trinitrotoluene a Threshold Limit Value of 0.5 mg/m^3 with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trinitrotoluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to trinitrotoluene can cause liver damage with yellow jaundice and anemia which may be fatal. It may also cause irritation of the eyes, nose, and throat with sneezing, cough, and sore throat. It may cause a skin rash and stain the skin, hair, and nails a yellowish color. It may affect the ability of the blood to carry oxygen. This may result in a bluish discoloration of the skin, weakness, drowsiness, shortness of breath and unconsciousness. In addition, it may cause muscular pains, heart irregularities, kidney irritation, cataracts of the eyes, menstrual irregularities, and nerve damage.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to trinitrotoluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to trinitrotoluene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to trinitrotoluene would be expected to be at increased risk from exposure. Examination of the blood, liver, eyes, cardiovascular system, nervous system, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Trinitrotoluene has been shown to cause aplastic anemia in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Liver function tests: Since liver damage has been observed in humans exposed to trinitrotoluene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has been observed in humans exposed to trinitrotoluene, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on a semi-annual basis.

- **Summary of toxicology**

Trinitrotoluene (TNT) dust or fume causes liver

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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damage, aplastic anemia, cyanosis, and dermatitis. There have been numerous fatalities of workers exposed to TNT in munitions plants; in a series of 22 fatal cases, 8 died from toxic hepatitis, 13 from aplastic anemia, and 1 from a combination of both. The vapor or dust can cause irritation of mucous membranes, resulting in sneezing, cough, and sore throat. Although intense or prolonged exposure to TNT may cause some cyanosis, it is not regarded as a strong producer of methemoglobin. Other occasional effects are leukocytosis or leukopenia, peripheral neuritis, muscular pains, cardiac irregularities, and renal irritation. Cataracts have been observed in a considerable proportion of chronically exposed workers; one report indicates that 26 of 61 workers with an average exposure of 8.4 years had a characteristic peripheral cataract. TNT causes sensitization dermatitis; the hands, wrists, and forearms are most commonly affected, but skin at friction points such as the collar line, belt line, and ankles is also often involved; erythema, papules, and an itchy eczema can be severe. The skin, hair, and nails of exposed workers may be stained yellow.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 227
2. Boiling point (760 mm Hg): 240 C (464 F) (explodes)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of trinitrotoluene): Not applicable
5. Melting point: 81 C (178 F)
6. Vapor pressure at 85 C (185 F): 0.053 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.013
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Slow decomposition occurs above 180 C (356 F). Exposure to light may increase impact sensitivity. Rapid heating may cause detonation.
2. Incompatibilities: Contact with strong oxidizers may cause fire. Contact with ammonia or with strong alkalies may increase sensitivity to shock. Can react vigorously with oxidizable materials.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving trinitrotoluene.
4. Special precautions: Protect from shock.

- **Flammability**

1. Flash point: Explodes
2. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): 100 cm
3. Explosion temperature (temperature required to cause explosion in five seconds): 475 C (887 F)
4. Extinguishant: Water may be used on small fires. Do not attempt to extinguish large fires.

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of TNT.
2. Eye Irritation Level: Grant states that "irritation of the eyes and skin is not uncommon among munitions workers exposed to its dust and fumes." No quantitative information is available concerning the air concentrations which produce the eye irritation.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of TNT, this substance is treated as a material with poor warning properties. The concentration in saturated air at 20 C might result in a significant exposure relative to the permissible exposure.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for trinitrotoluene had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid trinitrotoluene or liquids containing trinitrotoluene.
- If employees' clothing may have become contaminated with solid trinitrotoluene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which may have become contaminated with solid trinitrotoluene or liquids containing trinitrotoluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of trinitrotoluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the trinitrotoluene, the person performing the operation should be informed of trinitrotoluene's hazardous properties.
- Non-impervious clothing which becomes contaminated with trinitrotoluene should be removed promptly and not reworn until the trinitrotoluene is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid trinitrotoluene or liquids containing trinitrotoluene may contact the eyes.

SANITATION

- Workers subject to skin contact with solid trinitrotoluene or liquids containing trinitrotoluene should wash with soap or mild detergent and water any areas of the body which may have contacted trinitrotoluene at the end of each work day.
- Skin that becomes contaminated with trinitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any trinitrotoluene.
- Eating and smoking should not be permitted in areas where solid trinitrotoluene or liquids containing trinitrotoluene are handled, processed, or stored.
- Employees who handle solid trinitrotoluene or liquids containing trinitrotoluene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to trinitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of shells, bombs, grenades, and mines; use in commercial explosives, and propellant compositions	Process enclosure; local exhaust ventilation; personal protective equipment
Use in the production of intermediates for synthesis of dyestuffs and photographic chemicals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If trinitrotoluene or liquids containing trinitrotoluene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If trinitrotoluene or liquids containing trinitrotoluene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If trinitrotoluene or liquids containing trinitrotoluene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of trinitrotoluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When trinitrotoluene or liquids containing trinitrotoluene have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If trinitrotoluene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Attempt to reclaim spilled material; however, do not sweep or burn unless this is supervised by explosives experts.

- Waste disposal method:

Trinitrotoluene may be disposed of only by explosives experts.

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RESPIRATORY PROTECTION FOR TRINITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 1.5 mg/m³
Particulate or Vapor Concentration	
15 mg/m³ or 1.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
75 mg/m³ or 7.5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3000 mg/m³ or 300 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3000 mg/m³ or 300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Triorthocresyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3C_6H_4O)_3PO$
- Synonyms: O-tritolyl phosphate; TCP; TOCP
- Appearance and odor: Colorless, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for triorthocresyl phosphate is 0.1 milligram of triorthocresyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Triorthocresyl phosphate can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Triorthocresyl phosphate may cause paralyses of the lower arms and legs if it is swallowed, inhaled (as a fog mist, or aerosol), or absorbed through the skin. Nausea, vomiting, diarrhea, and abdominal pain may occur shortly after exposure. These symptoms disappear and are followed, after a symptom-free period of 3 to 28 days, by the paralytic effect.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to triorthocresyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to triorthocresyl phosphate at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the peripheral and central nervous systems should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Triorthocresyl phosphate (TOCP) causes peripheral neuropathy with flaccid paralysis of the distal muscles of the upper and lower extremities, followed in some cases by a spastic paralysis. In affected cats and hens, extensive damage is observed in the spinal cord and sciatic nerves; damage to the myelin sheath and Schwann cells is secondary to the destructive lesion in the axon, which starts at the distal end of the longer axons. Thousands of people have been poisoned by the accidental ingestion of TOCP in contaminated foods and beverages; reports of intoxication from occupational exposure are rare. Shortly after ingestion there may be nausea, vomiting, diarrhea, and abdominal pain. After a symptom-free interval of 3 to 28 days, most patients complain of sharp, cramplike pains in the calf muscles, and some of numbness and tingling in the feet and sometimes the hands. Within a few hours there is increasing weakness of the legs and feet, progressing to bilateral footdrop. After an interval of another 10 days, weakness of the fingers and wristdrop develop, but the paralysis is not usually as severe as occurs in the feet and legs; this process does not extend above the elbows; the thigh muscles are infrequently involved. Sensory changes, if they occur, are minor. With severe intoxication, lesions of the anterior horn cells and the pyramidal

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tracts may also occur. Muscular weakness may increase over a period of several weeks or months; recovery may take months or years, and in 25 to 30% of cases permanent residual effects remain, usually confined to the lower limbs. Fatalities are rare and occur principally in those who have taken large quantities of TOCP in a short period of time; autopsy of six human cases revealed involvement of anterior horn cells and demyelination of nerve cells. The lethal dose for humans by ingestion is about 1.0 g/kg; severe paralysis has been produced by ingestion of 6 to 7 mg/kg. In workers engaged in the manufacture of aryl phosphates (including up to 20% TOCP) and exposed to concentrations of aryl phosphates at 0.2 to 3.4 mg/m^3, there was some inhibition of plasma cholinesterase but no correlation of this effect with degree of exposure or with minor gastrointestinal or neuromuscular symptoms. No effects on the eyes or skin have been reported; TOCP is readily absorbed through the skin without local irritant effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 368
2. Boiling point (760 mm Hg): 410 C (770 F) (decomposes)
3. Specific gravity (water = 1): 1.17
4. Vapor density (air = 1 at boiling point of triorthocresyl phosphate): Not applicable
5. Melting point: −33 C (−27 F)
6. Vapor pressure at 20 C (68 F): Very low (0.02 mm Hg at 150 C (302 F))
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00003
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving triorthocresyl phosphate.
4. Special precautions: Liquid triorthocresyl phosphate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 225 C (437 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Triorthocresyl phosphate (TOCP) is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of triorthocresyl phosphate on a filter, followed by extraction with ether, and gas chromatographic analysis. An analytical method for triorthocresyl phosphate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid triorthocresyl phosphate.
- Clothing contaminated with triorthocresyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of triorthocresyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the triorthocresyl phosphate, the person

performing the operation should be informed of triorthocresyl phosphate's hazardous properties.

- Non-impervious clothing which becomes contaminated with triorthocresyl phosphate should be removed promptly and not reworn until the triorthocresyl phosphate is removed from the clothing.

SANITATION

- Skin that becomes contaminated with triorthocresyl phosphate should be promptly washed or showered with soap or mild detergent and water to remove any triorthocresyl phosphate.
- Eating and smoking should not be permitted in areas where liquid triorthocresyl phosphate is handled, processed, or stored.
- Employees who handle liquid triorthocresyl phosphate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to triorthocresyl phosphate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a flame retarder and plasticizer in chlorinated rubber, nitrile rubber and resins; use in hot extrusion, molding, or bulk forming of plasticized polyvinyl chloride	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in coatings and adhesives based on plasticized cellulose esters and alkyds	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a gasoline additive to control pre-ignition	Personal protective equipment
Use as a hydraulic fluid and a heat exchange medium	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a synthetic lubricant; as a waterproofing agent; as a primary component of adhesives for air filter media; use as a solvent mixture for nitrocellulose and other natural resins	Personal protective equipment
Use as an extraction solvent in recovery of phenol from gas-plant effluents and coke-oven waste waters	Personal protective equipment
Use in grinding media for pigments; use as an intermediate in synthesis of pharmaceuticals	General dilution ventilation; process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid triorthocresyl phosphate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid triorthocresyl phosphate gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid triorthocresyl phosphate soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of triorthocresyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid triorthocresyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid triorthocresyl phosphate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Liquid triorthocresyl phosphate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR TRIORTHOCRESYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Triphenyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_6H_5O)_3PO$
- Synonyms: TPP; phenyl phosphate
- Appearance and odor: Colorless solid with a faint aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for triphenyl phosphate is 3 milligrams of triphenyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Triphenyl phosphate can affect the body if it is inhaled. It may also affect the body if it is swallowed.

- **Effects of overexposure**

Repeated exposure may cause minor changes in the blood enzymes. Animal exposures have produced muscle weakness and paralysis. These effects have not been reported in man.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to triphenyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to triphenyl phosphate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from triphenyl phosphate exposure.

—Neuromuscular disorders: Triphenyl phosphate causes neurotoxic effects in animals. Persons with pre-existing neuromuscular disorders may be at increased risk.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Triphenyl phosphate is a neurotoxin in animals. When injected in cats it caused delayed paralysis. Two of 6 cats given a single intraperitoneal injection of triphenyl phosphate at 0.1 to 0.4 g/kg developed paralysis after 16 to 18 days. A group of 11 workers exposed to vapor, mist, or dust at an average concentration of 3.5 mg/m^3 and occasionally as high as 40 mg/m^3 for 8 to 10 years exhibited no signs of illness; the only positive finding was a slight but statistically significant reduction in erythrocyte cholinesterase activity. In workers engaged in the manufacture of aryl phosphates (including triphenyl phosphates and up to 20% triorthocresyl phosphate) and exposed to concentrations of aryl phosphates of 0.2 to 3.4 mg/m^3, there was some inhibition of plasma cholinesterase but no correlation of this effect with degree of exposure or with minor gastrointestinal or neuromuscular symptoms. The effects of triphenyl phosphate on the eye have not been reported; application in ethanol to the skin of mice produced no more irritation than was expected from the solvent.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 326
2. Boiling point (760 mm Hg): 370 C (698 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of triphenyl phosphate): Not applicable
5. Melting point: 48.5 C (119 F)
6. Vapor pressure at 20 C (68 F): Very low (0.15 mm

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Hg at 150 C (302 F))

7. Solubility in water, g/100 g water at 20 C (68 F): 0.001
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving triphenyl phosphate.
4. Special precautions: Liquid triphenyl phosphate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 220 C (428 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

Triphenyl phosphate is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of triphenyl phosphate on a filter, followed by extraction with ether, and gas chromatographic analysis. An analytical method for triphenyl phosphate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to triphenyl phosphate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a flame-retardant and plasticizer in compounding of chlorinated rubber; use on coatings and adhesives	General dilution ventilation; process enclosure; local exhaust ventilation
Use in hot extrusion, molding, or other bulk forming plasticized cellulose acetates	General dilution ventilation; process enclosure; local exhaust ventilation
Use as a fireproofing agent in manufacture of roofing paper	General dilution ventilation; process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of triphenyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When triphenyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If triphenyl phosphate is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

Triphenyl phosphate may be disposed of:

1. By making packages of triphenyl phosphate in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving triphenyl phosphate in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Triphenyl Phosphate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR TRIPHENYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 3 mg/m³
Particulate Concentration	
15 mg/m³ or less	Any dust and mist respirator, except single-use.
30 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
150 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Turpentine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_{16}$ (approximately); minimum alpha-pinene content 40% by weight
- Synonyms: Gum spirits of turpentine; turps; wood turpentine; spirits of turpentine; sulfate wood turpentine; sulfate turpentine; gum turpentine; steam-distilled turpentine
- Appearance and odor: Colorless liquid with a characteristic, paint odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for turpentine is 100 parts of turpentine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 560 milligrams of turpentine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Turpentine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to turpentine may cause irritation of the eyes, nose, throat, lungs, and skin. It may also cause headache, dizziness, and painful urination or dark-red urine. Greater exposure may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure causes skin irritation. Skin sensitization can occur.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to turpentine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to turpentine at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from turpentine exposure.

—Skin disease: Turpentine is a skin defatting agent and sensitizer and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although turpentine is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Turpentine has been reported to cause albuminuria and hematuria in humans and special consideration should be given to those with a history of impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of turpentine might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Turpentine vapor is a mucous membrane irritant and, at higher concentrations, a convulsant. The LC50 for rats is 3590 ppm for 1 hour and 2150 ppm for 6 hours; hyperpnea, ataxia, tremors, and convulsions were noted. In cats, 1440 ppm produced disturbances in equilibrium and convulsions in 30 to 60 minutes; paralysis occurred in 150 to 180 minutes. In human subjects,

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750 to 1000 ppm for several hours caused irritation of the eyes, headache, dizziness, nausea, and tachycardia; 1878 ppm for 1 to 4 hours was considered definitely toxic. Heavy overexposure is also reported to cause irritation of the nose and throat, cough, headache, vertigo, and irritation of the kidneys and bladder manifested by transient albuminuria and hematuria. However, there is little evidence that turpentine vapor at lower concentrations is a chronic systemic poison. Liquid in the eye causes conjunctivitis and corneal burns; a vapor concentration of 75-200 ppm is said to be moderately irritating. The liquid is also a defatting agent and causes skin irritation. Some persons may develop skin hypersensitivity. Mild intoxication from skin absorption has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 136 (approximately)
2. Boiling point (760 mm Hg): 150 to 180 C (302 to 356 F)
3. Specific gravity (water = 1): 0.864
4. Vapor density (air = 1 at boiling point of turpentine): 4.7
5. Melting point: −50 to −60 C (−58 to −76 F)
6. Vapor pressure at 25 C (77 F): 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents (especially chlorine) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving turpentine.
4. Special precautions: Turpentine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 35 C (95 F) (closed cup)
2. Autoignition temperature: 253 C (488 F)
3. Flammable limits in air, % by volume: Lower: 0.8
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that "the odor of 200 ppm turpentine in air is readily noticeable."
2. Eye Irritation Level: Patty states that 200 ppm "is moderately irritating to the eyes and mucous membranes of the nasal passages."
3. Evaluation of Warning Properties: Through its odor and irritant effects, turpentine can be detected at a level within twice the permissible exposure limit. For the purposes of this guideline, turpentine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of turpentine vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure turpentine may be used. An analytical method for turpentine is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid turpentine.
- Clothing wet with liquid turpentine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of turpentine from the clothing. If the clothing is to be laundered or

otherwise cleaned to remove the turpentine, the person performing the operation should be informed of turpentine's hazardous properties.

- Any clothing which becomes wet with liquid turpentine should be removed immediately and non-impervious clothing which becomes contaminated with turpentine should be removed promptly and such clothing should not be reworn until the turpentine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid turpentine may contact the eyes.

SANITATION

- Skin that becomes contaminated with turpentine should be promptly washed or showered with soap or mild detergent and water to remove any turpentine.
- Employees who handle liquid turpentine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to turpentine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of synthetic pine oil; insecticides; and in beta-pinene resins, flavors, and perfumes	Local exhaust ventilation; process enclosure; personal protective equipment
Use in preparation of polishes; use in manufacture of synthetic camphor, and use in paints	Local exhaust ventilation; process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If turpentine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If turpentine gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If turpentine soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of turpentine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If turpentine has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If turpentine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Turpentine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Turpentine may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Turpentine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR TURPENTINE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
1900 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1900 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Uranium and Insoluble Compounds (as Uranium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all uranium and insoluble compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic uranium

- Formula: U
- Synonyms: None
- Appearance: Heavy, silvery white metal which is pyrophoric when finely divided.
- Note: U238 is radioactive with a half life of 4,900,000,000 years.

Uranium octaoxide

- Formula: U_3O_8
- Synonyms: Pitchblende
- Appearance and odor: Black, odorless solid.

Uranium tetrafluoride

- Formula: UF_4
- Synonyms: None
- Appearance and odor: Green, odorless solid.

Uranium hydride

- Formula: UH_3
- Synonyms: None
- Appearance: Brownish black or brownish gray powder.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for uranium or insoluble compounds is 0.25 milligram of uranium or insoluble compounds (as uranium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for uranium or insoluble compounds (as uranium) a Threshold Limit Value of 0.2 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Uranium or insoluble compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Exposure to insoluble uranium compounds has been reported to cause an increase in cancer of the lymphatic and blood-forming tissues in man. Prolonged contact with the skin might cause radiation damage to the skin. Prolonged inhalation of insoluble uranium compounds has caused damage to the lungs of animals.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to uranium or insoluble compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to uranium or insoluble compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Exami-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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nation of the respiratory system, blood, and lymphatic system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Since uranium is deposited in the bone and is an alpha particle emitter, the function of the bone marrow is at risk. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—14" x 17" chest roentgenogram: Uranium or insoluble compounds cause lung damage in animals. Surveillance of the lungs is indicated.

—Urinalysis: Although not reported with insoluble uranium compounds, kidney damage has been reported due to uranium exposure. A urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. In addition, a determination of urinary uranium levels should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Insoluble compounds of uranium are less toxic than the soluble compounds. They are weakly radioactive and are principally alpha particle emitters; fibrotic changes have been observed in the lungs of animals after prolonged inhalation exposure, although radiation effects (other than possible carcinogenesis from absorbed uranium) have not been observed in humans. Both feeding and percutaneous toxicity studies on animals indicate that the insoluble uranium compounds are less toxic than the soluble compounds. Repeated exposures of three animal species to uranium dioxide dust at a concentration of 5 mg uranium/m³ for periods up to 5 years resulted in no kidney injury; over 90% of the uranium found in the body was in the lungs and tracheobronchial lymph nodes (TLN). Fibrotic changes suggestive of radiation injury were seen occasionally in the TLN of dogs and monkeys and in the lungs of monkeys after exposure periods longer than 3 years; the estimated alpha dose to tissues was greater than 500 rads for lungs and 7000 rads for TLN. Rats injected with metallic uranium in the femoral marrow and in the chest wall developed sarcomata; whether this was due to metallocarcinogenic or radiocarcinogenic action could not be determined. The increased incidence of lung cancer reported among uranium miners is probably the result of exposure to radon gas and its particulate daughters, rather than to uranium dust. In a group of uranium mill workers, there was an excess of deaths from malignant disease of lymphatic and hematopoietic tissue; data from animal experiments suggested that this excess may have resulted from irradiation of lymph nodes by thorium-230, a disintegration product of uranium. Some absorbed uranium is deposited in bone; a potential risk of radiation effects on bone marrow has been postulated, but extensive clinical studies on exposed workers have disclosed no hematologic abnormalities. No evidence of chronic toxicity, either chemical or radiation, was observed for any uranium compound in the milling process during the first 6 years of the atomic energy program; all exposed workers were under very close medical surveillance. Prolonged skin contact with uranium compounds should be avoided because of potential radiation damage to basal cells; dermatitis has occurred as a result of handling uranium tetrafluoride.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Metallic uranium**

1. Molecular weight: 238.03
2. Boiling point (760 mm Hg): 3818 C (6904 F)
3. Specific gravity (water = 1): 18.95
4. Vapor density (air = 1 at boiling point of metallic uranium): Not applicable
5. Melting point: 1133 C (2071 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Uranium octaoxide**

1. Molecular weight: 842.1
2. Boiling point (760 mm Hg): Decomposes at 1300 C (2372 F)
3. Specific gravity (water = 1): 7.31
4. Vapor density (air = 1 at boiling point of uranium octaoxide): Not applicable
5. Melting point: 1300 C (2372 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1):

- **Physical data—Uranium tetrafluoride**

1. Molecular weight: 314
2. Boiling point (760 mm Hg): 1417 C (2582 F) (sublimes)
3. Specific gravity (water = 1): 6.7
4. Vapor density (air = 1 at boiling point of uranium tetrafluoride): Not applicable
5. Melting point: 969 C (1776 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Uranium hydride**

1. Molecular weight: 241
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of uranium hydride): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero, except for decomposition products

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat (uranium hydride). Uranium turnings and fines stored out-of-doors in closed containers under water or water-soluble oil will partially convert into the hydride and eventually ignite during hot weather.

2. Incompatibilities: Contact of uranium with carbon dioxide, carbon tetrachloride, or nitric acid will cause fires or explosions. Contact of uranium hydride with strong oxidizers may cause fires and explosions. Contact of uranium hydride with water will form flammable and explosive hydrogen gas. Contact of uranium hydride with halogenated hydrocarbons can be violent.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and carbon monoxide) may be released when uranium or insoluble compounds decompose.

4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable

2. Minimum ignition temperature: Uranium: 20 C (68 F) (cloud); 100 C (212 F) (layer); Uranium hydride: 20 C (68 F) (cloud); 20 C (68 F) (layer)

3. Minimum explosive concentration: 60 grams/m^3

4. Extinguishant: Dry powder, dry sand, graphite

- **Warning properties**

According to Grant, "several uranium compounds tested by dropping on the eyes of rabbits, guinea pigs, and rats have been found to cause severe eye damage as well as systemic poisoning. Compounds which have been found to cause moderately severe injury of the eyes are . . . uranium tetrafluoride, . . . uranium trioxide, uranium dioxide, and uranium peroxide . . . . The mildest damage was caused by the various uranium oxides."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for uranium or insoluble compounds had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing uranium or insoluble compounds.
- If employees' clothing may have become contaminated with solids or liquids containing uranium or insoluble compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with uranium or insoluble compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of uranium or insoluble compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the uranium or insoluble compounds, the person performing the operation should be informed of the hazardous properties of these substances.
- Non-impervious clothing which becomes contaminated with uranium or insoluble compounds should be removed promptly and not reworn until the uranium or insoluble compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing uranium or insoluble compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solids or liquids containing uranium or insoluble compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with uranium or insoluble compounds should be promptly washed or showered with soap or mild detergent and water to remove any uranium or insoluble compounds.
- Eating and smoking should not be permitted in areas where solids or liquids containing uranium or insoluble compounds are handled, processed, or stored.
- Employees who handle solids or liquids containing uranium or insoluble compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to uranium or insoluble compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, grinding, and milling of ores	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use of insoluble compounds as chemical intermediates in preparation of uranium compounds; use for nuclear technology	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in nuclear reactors as fuel and to pack nuclear fuel rods	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from burning of uranium metal chips and smelting operations	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in ceramics industry for pigments, coloring porcelain, painting on porcelain, and enamelling	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as catalysts for many reactions; in production of fluorescent glass	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solids or liquids containing uranium or insoluble compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solids or liquids containing uranium or insoluble compounds get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing uranium or insoluble compounds penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of uranium or insoluble compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solids or liquids containing uranium or insoluble compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If uranium or insoluble compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation. Liquid containing uranium or insoluble compounds should be absorbed in vermiculite, dry sand, earth, or a similar material. Uranium chips or turnings which are spilled should be covered with oil.

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RESPIRATORY PROTECTION FOR URANIUM AND INSOLUBLE COMPOUNDS (AS URANIUM)

Condition	Minimum Respiratory Protection* Required Above 0.25 mg/m³
Particulate Concentration	
2.5 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator approved fo radon daughters or radionuclides. Any supplied-air respirator. Any self-contained breathing apparatus.
12.5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
30 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 30 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Uranium Compounds (as Uranium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble uranium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Uranium hexafluoride

- Formula: UF_6
- Synonyms: None
- Appearance: Yellow, deliquescent solid.

Uranyl nitrate

- Formula: $UO_2(NO_3)_2\text{-}6H_2O$
- Synonyms: Uranium nitrate
- Appearance and odor: Yellow, odorless solid.

Uranyl sulfate

- Formula: $UO_2SO_4\text{-}3H_2O$
- Synonyms: None
- Appearance and odor: Yellow-green, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble uranium compounds is 0.05 milligram of soluble uranium compounds (as uranium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for soluble uranium compounds a Threshold Limit Value of 0.2 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble uranium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble uranium compounds may cause irritation of the eyes with damage, lung damage, and kidney damage.

2. Long-term Exposure: Repeated or prolonged skin exposure to soluble uranium compounds may cause radiation damage to the skin. Exposure to soluble uranium compounds has been reported to cause an increase in cancer of the lymphatic and blood-forming tissues of man.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble uranium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble uranium compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, blood, liver, lymphatic system, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to uranium, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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—A complete blood count: Since uranium is deposited in the bone and is an alpha-particle emitter, the function of the bone marrow should be monitored. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. In addition, a determination of urinary uranium levels should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Soluble compounds of uranium as dust or mist are respiratory irritants and are toxic to the kidneys; uranium is weakly radioactive and emits alpha particles. Animals repeatedly exposed to dusts of soluble uranium compounds in concentrations from 3 to 20 mg/m^3 died of pulmonary and renal damage; both feeding and percutaneous toxicity studies on animals indicate that the more soluble compounds are the most toxic. In animals, effects on the liver are a consequence of the acidosis and azotemia induced by renal dysfunction. Rats injected with metallic uranium in the femoral marrow and in the chest wall developed sarcomata; whether this was due to metallocarcinogenic or radiocarcinogenic action could not be determined. The increased incidence of lung cancer reported among uranium miners is probably the result of exposure to radon gas and its particulate daughters, rather than to uranium dust. In a group of uranium mill workers there was an excess of deaths from malignant disease of lymphatic and hematopoietic tissue; data from animal experiments suggested that this excess may have resulted from irradiation of lymph nodes by thorium-230, a disintegration product of uranium. Some absorbed uranium is deposited in bone; a potential risk of radiation effects on bone marrow has been postulated, but extensive clinical studies on exposed workers have disclosed no hematologic abnormalities. Accidental exposure of workers to a mixture of uranium hexafluoride, uranium oxyfluoride, hydrofluoric acid, and live steam caused lacrimation, conjunctivitis, shortness of breath, paroxysmal cough, rales in the chest, nausea, vomiting, skin burns, transitory albuminuria, and elevation of blood urea nitrogen. The persons having the greatest exposure showed the highest urinary uranium levels; in addition, their urinary abnormalities were the most severe; these were albuminuria plus red cells and casts in the urinary sediment. Blood urea nitrogen remained elevated for several weeks. The injurious effects observed on the skin, eyes, and respiratory tract apparently were caused by the irritant action of the fluoride ion, whereas the uranium was responsible for the transient renal changes. No evidence of chronic toxicity, either chemical or radiation, was observed for any uranium compound during the first 6 years of the atomic energy program; all exposed workers were under very close medical surveillance. Soluble uranium compounds tested on the eyes of animals caused severe eye damage as well as systemic poisoning; the anion and its hydrolysis products determine the degree of injury. A hot nitric acid solution of uranyl nitrate spilled on the skin caused skin burns, nephritis, and encephalopathy. Prolonged skin contact with uranium compounds should be avoided because of potential radiation damage to basal cells; dermatitis has occurred as a result of handling uranium hexafluoride.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Uranium hexafluoride**

1. Molecular weight: 352
2. Boiling point (760 mm Hg): 56 C (133 F) (sublimes)
3. Specific gravity (water = 1): 4.68
4. Vapor density (air = 1 at boiling point of uranium hexafluoride): 12 (approximately)
5. Melting point: 65 C (149 F)
6. Vapor pressure at 20 C (68 F): 109 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Uranyl nitrate**

1. Molecular weight: 502.1
2. Boiling point (760 mm Hg): 118 C (244 F)
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of uranyl nitrate): Not applicable
5. Melting point: 60.2 C (140 F) (loses water)
6. Vapor pressure at 20 C (68 F): None, except water of crystallization
7. Solubility in water, g/100 g water at 20 C (68 F): 67
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Uranyl sulfate**

1. Molecular weight: 420.1
2. Boiling point (760 mm Hg): Decomposes at 100 C (212 F) (loses water)
3. Specific gravity (water = 1): 3.3
4. Vapor density (air = 1 at boiling point of uranyl sulfate): Not applicable
5. Melting point: 100 C (212 F) (loses water)
6. Vapor pressure at 20 C (68 F): None, except water of crystallization
7. Solubility in water, g/100 g water at 20 C (68 F): 70
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of uranyl nitrate with combustible material may cause fires and explosions. Uranium hexafluoride reacts with water to form hydrofluoric acid, a very corrosive substance.
3. Hazardous decomposition products: Toxic gases

and vapors (such as oxides of nitrogen and hydrofluoric acid) may be released in a fire involving soluble uranium compounds.

4. Special precautions: Uranium hexafluoride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Grant states that "several uranium compounds tested by dropping on the eyes of rabbits, guinea pigs, and rats have been found to cause severe eye damage as well as systemic poisoning. Compounds which have been found to cause moderately severe injury of the eyes are uranium pentachloride, uranium tetrachloride, uranyl nitrate, (and) uranyl fluoride .... Application of 1 mg of solid uranium pentachloride to the eyes of rabbits caused the most severe necrosis of conjunctivae and lids, and perforating ulceration of the cornea. The other chlorides and the nitrate were also severely damaging."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for soluble uranium compounds had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solids or liquids containing uranium hexafluoride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing soluble uranium compounds.
- If employees' clothing has had any possibility of being contaminated with uranium hexafluoride, or if employees' clothing may have become contaminated with other soluble uranium compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with uranium hexafluoride or clothing contaminated with other soluble uranium compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of soluble uranium compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the soluble uranium compounds, the person performing the operation should be informed of soluble uranium compounds's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solids or liquids containing uranium hexafluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with uranium hexafluoride should be removed immediately and non-impervious clothing which becomes contaminated with other soluble uranium compounds should be removed promptly and not reworn until the soluble uranium compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing soluble uranium compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solids or liquids containing soluble uranium compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with uranium hexafluoride should be immediately washed or showered and skin that becomes contaminated with soluble uranium compounds should be promptly washed or showered to remove any soluble uranium compounds.

- Workers subject to skin contact with solids or liquids containing uranium hexafluoride should wash any areas of the body which may have contacted uranium hexafluoride at the end of each work day.
- Eating and smoking should not be permitted in areas where solids or liquids containing soluble uranium compounds are handled, processed, or stored.
- Employees who handle solids or liquids containing soluble uranium compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble uranium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining and purification of ore; during enrichment of elemental uranium; from recovery of process waste	Process enclosure; local exhaust ventilation; personal protective equipment
Use in fabrication of materials for military use and power plants	Process enclosure; local exhaust ventilation; personal protective equipment
Use as analytical reagents; use in chemical synthesis; use in manufacture of dyestuff intermediates and preparation of oxides	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of ceramic glazes; use as photographic intensifiers and in x-ray technology; in miscellaneous uses for textile printing, tobacco printing, antifungal agents, electroplating additives, and bacterial oxidants	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solids or liquids containing soluble uranium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solids or liquids containing soluble uranium compounds get on the skin, immediately flush the contaminated skin with water. If solids or liquids containing soluble uranium compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble uranium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When solids or liquids containing soluble uranium compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If soluble uranium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble uranium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

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RESPIRATORY PROTECTION FOR URANIUM SOLUBLE COMPOUNDS (AS URANIUM)

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m^3
Particulate Concentration	
2.5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece (not applicable for uranium halides). A chemical cartridge respirator with a full facepiece, acid gas cartridge(s), and high efficiency particulate filter (for uranium halides only). A gas mask with a chin-style or a front- or back-mounted acid gas canister and high efficiency particulate filter (for uranium halides only). Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter (not applicable for uranium halides). A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with acid gas cartridge for uranium halides. Any gas mask providing protection against acid gases and particulates (for uranium halides only). Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Vanadium Pentoxide Dust

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: V_2O_5
- Synonyms: None
- Appearance and odor: Yellow-orange powder or dark gray flakes with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for vanadium pentoxide dust is a ceiling of 0.5 milligrams of vanadium pentoxide dust per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 0.05 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Vanadium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Vanadium pentoxide dust can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Vanadium pentoxide dust may cause irritation of the eyes, nose, throat, and respiratory tract. It may also cause bronchitis with wheezing and chest pain. A greenish discoloration of the tongue may occur.

2. Long-term Exposure: After symptoms have occurred following short-term exposure, repeated exposure may cause more severe symptoms of the same nature. In addition, repeated exposure may cause chronic bronchitis. Repeated or prolonged exposure may also cause an allergic skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to vanadium pentoxide dust.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to vanadium pentoxide dust at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Vanadium pentoxide dust may cause respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Vanadium pentoxide dust is reported to cause asthmatic-like symptoms. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing. Vanadium in the urine may be evidence of absorption and excretion of this element since vanadium is not normally found in human urine.

- **Summary of toxicology**

Vanadium pentoxide dust is a respiratory and eye irritant. Sixteen workers exposed to concentrations of dust (and possibly some fume) in excess of 0.5 mg/m^3 with a mean particle size in the micron and submicron range developed conjunctivitis, nasopharyngitis, hacking cough, fine rales, and wheezing; in three workers exposed to the highest concentrations, the onset of symptoms occurred at the end of the first workday. The

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bronchospastic element in the more seriously ill persisted for 48 hours after removal from exposure; rales lasted for 3 to 7 days, and in several cases cough lasted for up to 14 days. Among those with acute intoxication there was increased severity of symptoms from subsequent exposures of lesser time and intensity. Urinary vanadium excretion was detectable in 12 of the workers for periods of up to 2 weeks; vanadium in the urine may be evidence of absorption and excretion of this element, since vanadium is not ordinarily found in human urine. Workers exposed to a mixture of ammonium metavanadate and vanadium pentoxide at concentrations near 0.25 mg/m^3 developed green tongue, metallic taste, throat irritation, and cough. Another report of 36 workers examined 8 years after an acute respiratory reaction from vanadium pentoxide exposure indicated no evidence of either pneumoconiosis or emphysema, although six still had bronchitis with rhonchi resembling asthma and bouts of dyspnea. Two volunteers exposed to a concentration of 1 mg/m^3 for 8 hours developed a persistent cough which lasted for 8 days; 21 days after the original exposure, re-exposure for 5 minutes to a heavy cloud of vanadium pentoxide dust occurred, and within 16 hours marked cough developed; the following day, rales and expiratory wheezes were present throughout the entire lung field, but pulmonary functions were normal. Subjects exposed to a concentration of 0.2 mg/m^3 for 8 hours developed a loose cough the following morning; others exposed for 8 hours to 0.1 mg/m^3 developed slight cough with increased mucus which lasted 3 to 4 days. Both eyes and skin are irritated by the dust or by contact with an acid solution of vanadium pentoxide; eczematous lesions have occurred, and in three cases there was an allergic response to patch tests with sodium vanadate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 181.9
  2. Boiling point (760 mm Hg): 1750 C (3182 F) (decomposes)
  3. Specific gravity (water = 1): 3.36
  4. Vapor density (air = 1 at boiling point of vanadium pentoxide dust): Not applicable
  5. Melting point: 690 C (1274 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not ocmbustible

- **Warning properties**

According to Grant, vanadium pentoxide dust "causes a sensation of burning and irritation of the eyes, and signs of conjunctivitis . . . ." The eye irritation is accompanied by "irritation of the nose and throat. The respiratory irritation occurs at lower concentrations than does the ocular irritation. The local effects on the eye have also been observed in rabbits." The *Documentation of TLV's* states that "Gulko referred to eye and bronchial irritation from exposure at 0.5 to 2.2 mg/m^3."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of vanadium pentoxide dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vanadium pentoxide dust on a mixed cellulose ester membrane filter, followed by chemical treatment and atomic desorption spectrophotometric analysis. An analytical method for vanadium pentoxide dust is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1). ical Methods for Set 1" (order number PB 271 712).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with vanadium pentoxide dust.
- Non-impervious clothing which becomes contaminated with vanadium pentoxide dust should be removed promptly and not reworn until the vanadium pentoxide dust is removed from the clothing.
- Clothing contaminated with vanadium pentoxide dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of vanadium pentoxide dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the vanadium pentoxide dust, the person performing the operation should be informed of vanadium pentoxide dust's hazardous properties.
- Employees should be provided with and required to use dust-resistant safety goggles where vanadium pentoxide dust may contact the eyes.

SANITATION

- Skin that becomes contaminated with vanadium pentoxide dust should be promptly washed or showered to remove any vanadium pentoxide dust.
- Eating and smoking should not be permitted in areas where vanadium pentoxide dust is generated in the handling, processing, or storing of vanadium pentoxide.
- Employees who handle vanadium pentoxide dust should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to vanadium pentoxide dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from cleaning and maintenance of furnaces, boilers, and gas turbines	Local exhaust ventilation; personal protective equipment
Liberation from mining and processing of ores; extraction from slag	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from use as a catalyst in the preparation of organic and inorganic compounds	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from chemical synthesis; use in manufacture of ultraviolet filter glass to prevent radiation injury and fading of fabrics	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from use in manufacture of afterburners for automobiles	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from use in textile industry as a catalyst to yield intensive black dyes; use in printing industry as a catalyst for formation of resinous black pigments from tar oils	Local exhaust ventilation
Liberation from use in ceramics industry in manufacture of ceramic pigments	Process enclosure; local exhaust ventilation
Liberation from use as a component of special steels in electric furnace steels, welding rods, and permanent magnets	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If vanadium pentoxide dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If vanadium pentoxide dust gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If vanadium pentoxide dust penetrates through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of vanadium pentoxide dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When vanadium pentoxide dust has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If vanadium pentoxide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation, or for disposal in a secured sanitary landfill.

- Waste disposal method:

Vanadium pentoxide dust may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Vanadium V," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Zenz, C., et al.: "Acute Vanadium Pentoxide Intoxication," *Archives of Environmental Health*, 5:542-546, 1962.

RESPIRATORY PROTECTION FOR VANADIUM PENTOXIDE DUST

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate Concentration	
25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
70 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 70 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Vanadium Pentoxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: V_2O_5
- Synonyms: None
- Appearance: Finely divided particulates dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for vanadium pentoxide fume is a ceiling of 0.1 milligrams of vanadium pentoxide fume per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 0.05 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Vanadium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Vanadium pentoxide fume can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Vanadium pentoxide fume may cause irritation of the eyes, nose, throat, and respiratory tract. It may also cause bronchitis with wheezing and chest pain. A greenish discoloration of the tongue may occur.

2. Long-term Exposure: After symptoms have occured following acute exposure, repeated exposure may cause more severe symptoms of the same nature. In addition, repeated exposure may cause chronic bronchitis. Repeated or prolonged exposure may cause an allergic skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to vanadium pentoxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to vanadium pentoxide fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Vanadium pentoxide fume may cause respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Vanadium pentoxide fume is reported to cause asthmatic-like symptoms. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Vanadium pentoxide fume is a respiratory and eye irritant; the fume is recognized as being generally more toxic than dust of larger particle size, so similar effects from fume could be expected at lower concentrations. Sixteen workers exposed to concentrations of dust (and possibly some fume) in excess of 0.5 mg/m^3 with a mean particle size in the micron and submicron range developed conjunctivitis, nasopharyngitis, hacking cough, fine rales, and wheezing; in three workers exposed to the highest concentrations, the onset of symptoms occurred at the end of the first workday. The

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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bronchospastic element in the more seriously ill persisted for 48 hours after removal from exposure; rales lasted for 3 to 7 days, and in several cases cough lasted for up to 14 days. Among those with acute intoxication there was increased severity of symptoms from subsequent exposures of lesser time and intensity. Urinary vanadium excretion was detectable in 12 of the workers for periods of up to 2 weeks; vanadium in the urine may be evidence of absorption and excretion of this element, since it is not ordinarily found in human urine. Workers exposed to a mixture of ammonium metavanadate and vanadium pentoxide at concentrations near 0.25 mg/m^3 developed green tongue, metallic taste, throat irritation, and cough. Another report of 36 workers examined 8 years after an acute respiratory reaction from vanadium pentoxide exposure indicated no evidence of either pneumoconiosis or emphysema, although six still had bronchitis with rhonchi resembling asthma and bouts of dyspnea. Two volunteers exposed to dust at a concentration of 1 mg/m^3 for 8 hours developed persistent cough which lasted for 8 days; 21 days after the original exposure, re-exposure for 5 minutes to a heavy cloud of vanadium pentoxide dust occurred, and within 16 hours marked cough developed; the following day, rales and expiratory wheezes were present throughout the entire lung field, but pulmonary functions were normal. Subjects exposed to dust at a concentration of 0.2 mg/m^3 for 8 hours developed a loose cough the following morning; others exposed for 8 hours to 0.1 mg/m^3 developed slight cough with increased mucus which lasted 3 to 4 days. Both eyes and skin are irritated by the dust or by contact with an acid solution of vanadium pentoxide; eczematous lesions have occurred, and in three cases there was an allergic response to patch tests with sodium vanadate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 181.9
  2. Boiling point (760 mm Hg): 1750 C (3182 F) (for solid)
  3. Specific gravity (water = 1): 3.36 (for solid)
  4. Vapor density (air = 1 at boiling point of vanadium pentoxide fume): Not applicable
  5. Melting point: 690 C (1274 F) (for solid)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible

- **Warning properties**

By analogy to vanadium pentoxide dust, which "causes a sensation of burning and irritation of the eyes and signs of conjunctivitis," according to Grant, vanadium pentoxide fume is treated as an eye irritant for the purposes of this guideline. The *Documentation of TLV's* states that "Gulko referred to eye . . . irritation from exposures at 0.5 to 2.2 mg/m^3" V_2O_5 dust.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of vanadium pentoxide fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vanadium pentoxide fume on a mixed cellulose ester membrane filter, followed by chemical treatment and atomic desorption spectrophotometric analysis. An analytical method for vanadium pentoxide fume is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

- Zenz, C., and Berg, B. A.: "Human Responses to Controlled Vanadium Pentoxide Exposure," *Archives of Environmental Health,* 14:709-712, 1967.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with vanadium pentoxide fume.
- Employees should be provided with and required to use dust-resistant safety goggles where vanadium pentoxide fume may contact the eyes.

SANITATION

- Eating and smoking should not be permitted in areas where vanadium pentoxide fume is generated in the handling, processing, or storing of vanadium pentoxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to vanadium pentoxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from production of pellets from electric furnaces	Local exhaust ventilation; personal protective equipment
Liberation from fabrication of alloys for use as an additive in special steels	Local exhaust ventilation; personal protective equipment
Liberation from metallurgical processes in furnaces	Process enclosure
Liberation from manufacture of semiconductors fused with sodium oxide	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of vanadium pentoxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of vanadium pentoxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

ADDITIONAL INFORMATION

To find additional information on vanadium pentoxide fume, look up vanadium pentoxide fume in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Vanadium (August 1977)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Vanadium V," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Hudson, T. G. F.: *Vanadium, Toxicology and Biological Significance*, Elsevier, New York, 1964.
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- Zenz, C., et al.: "Acute Vanadium Pentoxide Intoxication," *Archives of Environmental Health*, 5:542-546, 1962.

RESPIRATORY PROTECTION FOR VANADIUM PENTOXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate Concentration	
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
70 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 70 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR VINYL CHLORIDE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about vinyl chloride for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_3Cl
- **Structure:** $CH_2{=}CHCl$
- **Synonyms:** Chlorethene, chlorethylene, monochlorethylene, chloroethylene
- **Identifiers:** CAS 75-01-4; RTECS KU9625000; DOT 1086, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with a sweet odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 62.50
2. Boiling point (at 760 mmHg): -14°C (7°F)
3. Specific gravity (water = 1): 0.9121
4. Vapor density (air = 1 at boiling point of vinyl chloride): 2.15
5. Melting point: -155.7°C (-243.4°F)
6. Vapor pressure at 20°C (68°F): 2,580 mmHg
7. Solubility in water, g/100 g water at 24°C (75°F): 0.11
8. Ionization potential: 9.995 eV

- **Reactivity**

1. Incompatibilities: Atmospheric oxygen and strong oxidizers may react with vinyl chloride to produce peroxide, which can initiate a violent polymerization reaction.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride and carbon monoxide) may be released in a fire involving vinyl chloride.
3. Caution: Check valves for leaks.

- **Flammability**

1. Flash point: -78°C (-108°F) (open cup)
2. Autoignition temperature: 472°C (882°F)
3. Flammable limits in air, % by volume: Lower, 3.6; Upper, 33.0
4. Class IA Flammable Liquid Gas (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 3,000 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for vinyl chloride is 1 part of vinyl chloride per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift, and the ceiling concentration which shall at no time be exceeded is 5 ppm as determined in any 15-minute sampling period. The National Institute for Occupational Safety and Health (NIOSH) recommends that vinyl chloride be controlled and handled as a potential human carcinogen in the workplace, and the NIOSH recommended exposure limit (REL) is that exposure be minimized to the lowest feasible limit. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated vinyl chloride as an A1 substance (suspected human carcinogen) with an assigned threshold limit value, TLV® of 5 ppm [10 milligrams of vinyl chloride per cubic meter of air (mg/m^3)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

1988

Table 1.—Occupational exposure limits for vinyl chloride

	Exposure limits ppm	mg/m³
OSHA PEL TWA	1	—
Ceiling (15 min)	5	—
NIOSH REL (Ca)*	Lowest feasible limit	
ACGIH TLV® TWA (Ala)†	5	10

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (Ala): Human carcinogen with an assigned TLV.

HEALTH HAZARD INFORMATION

• Routes of exposure
Vinyl chloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* Acute inhalation of vinyl chloride by multiple species of animals caused central nervous system depression, coma, and death; acute inhalation by dogs also caused cardiac arrhythmias. In mice, rats, and hamsters, chronic inhalation or oral administration of vinyl chloride produced cancers of the liver, kidney, central nervous system, skin, and mammary and ear duct glands.
2. *Effects on humans:* Acute exposure of workers to vinyl chloride has caused narcotic and anesthetic effects. Repeated exposure of workers to vinyl chloride has caused increased blood pressure, decreased blood platelet counts, increased liver enzyme levels, restricted blood flow, bone degeneration in the fingers, liver and spleen enlargement, nervous system disturbances, central nervous system depression, decreased respiratory function, and emphysema. Cancer of the liver has been associated with exposure of workers to vinyl chloride during the polyvinyl chloride production process. Cancers of the lung, brain, skin, nervous system, gall bladder, mouth, and pharynx have also been observed in workers with a history of exposure to vinyl chloride. An increase in fetal mortality has been reported among wives of workers who had been exposed to vinyl chloride.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to vinyl chloride can cause dizziness, light-headedness, nausea, dullness of visual and auditory responses, drowsiness, and unconsciousness. Irritation of the skin and eyes can also occur. Skin contact with the liquid can cause frostbite.
2. *Long-term (chronic):* Exposure to vinyl chloride can cause thickening of the skin, contact and allergic dermatitis, fatigue, coughing and sneezing, abdominal pain, gastrointestinal bleeding, nausea, vomiting, indigestion, diarrhea, jaundice, weight loss, anorexia, and a cold and tingling sensation of the hands and feet.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including the employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to vinyl chloride, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, kidneys, and cardiovascular, hematopoietic (blood cell forming), nervous, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to vinyl chloride. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for serological tests of liver function and markers for infection with Hepatitis B virus.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations

should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to vinyl chloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, kidneys, and cardiovascular, hematopoietic, nervous, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following test should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and test of lung function.

- **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to vinyl chloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

Delayed-onset SHE's include: Liver cancer (hemangiosarcoma) and "white finger" (Raynaud's syndrome, secondary to vasculitis)

MONITORING AND MEASUREMENT PROCEDURES

- **Method**

Sampling and analysis may be performed by collecting vinyl chloride vapors with tandem charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure vinyl chloride may also be used if available. A detailed sampling and analytical method for vinyl chloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1007).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with vinyl chloride.

SANITATION

Clothing which is contaminated with vinyl chloride should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of vinyl chloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of vinyl chloride's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with vinyl chloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle vinyl chloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to vinyl chloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for vinyl chloride

Operations	Controls
During the manufacture of monomer, polymer, copolymer, and terpolymer	Process enclosure, personal protective equipment
During the transfer of monomer to tank cars or polymerization reactors; during maintenance work on tanks or reactors	Local exhaust ventilation, personal protective equipment
During the cleaning of polymerization reaction tanks	Process enclosure, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures:

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to vinyl chloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

If vinyl chloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to vinyl chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If vinyl chloride gets on the skin, wash it immediately with soap and water. If vinyl chloride penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If vinyl chloride is spilled or leaked, the following steps should be taken:

1. Stop the flow of gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for vinyl chloride

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted canister providing protection against the compound of concern Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

* U.S. GOVERNMENT PRINTING OFFICE:1993-750-004/80503

Occupational Health Guideline for Vinyl Toluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3C_6H_4CH=CH_2$
- Synonyms: Methylstyrene; tolylethylene; meta- and para-vinyltoluene (mixed isomers)
- Appearance and odor: Colorless liquid with a strong, disagreeable odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for vinyl toluene is 100 parts of vinyl toluene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 480 milligrams of vinyl toluene per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for vinyl toluene from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Vinyl toluene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Vinyl toluene may cause irritation of the nose, throat, eyes, and skin. It may also cause drowsiness.

2. Long-term Exposure: Repeated exposure may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to vinyl toluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to vinyl toluene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from vinyl toluene exposure.

—Kidney disease: Although vinyl toluene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of vinyl toluene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although vinyl toluene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: Vinyl toluene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The main toxic effect of vinyl toluene is irritation of the eyes, upper respiratory tract, and skin. With prolonged and repeated contact and absorption of high doses, there may be depression of the central nervous system.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 118
2. Boiling point (760 mm Hg): 168 C (334 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of vinyl toluene): 4.1
5. Melting point: −77 C (−106 F)
6. Vapor pressure at 20 C (68 F): 1.1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.009
8. Evaporation rate (butyl acetate = 1): Less than 0.5

- **Reactivity**

1. Conditions contributing to instability: Vinyl toluene is stabilized by a polymerization inhibitor (10 to 50 ppm of tert-butylcatechol). If this is not present in adequate concentrations, vinyl toluene can polymerize and explode in the container.
2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions. Also, catalysts for vinyl polymerization, such as peroxides, strong acids, and aluminum chloride should be avoided.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving vinyl toluene.
4. Special precautions: None

- **Flammability**

1. Flash point: 53 C (127 F) (closed cup)
2. Autoignition temperature: 495 C (923 F)
3. Flammable limits in air, % by volume: Lower: 0.1; Upper: 11
4. Extinguishant: Dry chemical, carbon dioxide, or foam.

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of vinyl toluene.
2. Irritation Levels: According to the ILO, vinyl toluene "gives rise to irritation of the nasal and conjunctival mucosae at 400 ppm and is detectable at 50 ppm."
3. Evaluation of Warning Properties: Since the ILO reports that vinyl toluene is detectable at a concentration below the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vinyl toluene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure vinyl toluene may be used. An analytical method for vinyl toluene is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid vinyl toluene.
- Clothing wet with liquid vinyl toluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of vinyl toluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the vinyl toluene, the person performing the operation should be informed of vinyl toluene's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid vinyl toluene should be removed promptly and not reworn until the vinyl toluene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid vinyl toluene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid vinyl toluene should be promptly washed or showered with soap or mild detergent and water to remove any vinyl toluene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to vinyl toluene may occur and control methods which may be effective in each case:

Operation	Controls
Use during spray applications of vinyl toluene polyester surface coatings	Local downdraft ventilation; personal protective equipment
Liberation during preparation of unsaturated polyester resins and alkyd coatings	Local downdraft ventilation
Use during application of specialty paints and varnishes	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of thermoplastic moldings via extrusion, injection, stamping, or other processes	Local downdraft ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If vinyl toluene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If vinyl toluene gets on the skin, promptly flush the contaminated skin with water. If vinyl toluene soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of vinyl toluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If vinyl toluene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If vinyl toluene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid. Vinyl toluene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Vinyl toluene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid.

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RESPIRATORY PROTECTION FOR VINYL TOLUENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
400 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Warfarin

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{19}H_{16}O_4$
- Synonyms: 3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin; WARF compound; compound 42; coumadin
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for warfarin is 0.1 milligram of warfarin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Warfarin can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Repeated exposure to warfarin may cause bleeding difficulties by impairing the clotting ability of the blood. Problems which may occur include easy bruising, nose bleeds, vomiting blood, bloody or tar-like stools, and bloody urine. A single large dose has been reported to be capable of causing bleeding problems after several days' delay.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to warfarin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to warfarin at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of blood disorders with bleeding tendencies would be expected to be at increased risk from exposure. Examination of the blood should be stressed.

—A complete blood count: Warfarin has been shown to cause hypoprothrombinemia in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Prothrombin time: Warfarin has been shown to cause hypoprothrombinemia in humans. A quick 1-stage prothrombin time or a thrombotest should be performed.

—Urinalysis: Warfarin has been shown to cause an increased bleeding tendency. A urinalysis should be obtained with emphasis on examination for red blood cells as an early indicator of internal bleeding.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Warfarin as the dust or in solution causes hypoprothrombinemia and vascular injury which results in internal hemorrhage. It suppresses the hepatic formation of prothrombin and of factors VII, IX, and X, causing a markedly reduced prothrombin activity of the blood; it also causes dilation and engorgement of blood vessels and an increase in capillary fragility. The inhibition of prothrombin formation does not become apparent until the prothrombin reserves are depleted, which usually requires exposure for a number of days. A single large

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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exposure may cause intoxication after a latency period of several days, but in a series of acute ingestion episodes there were no signs of hemorrhage or depression of plasma prothrombin. A farmer whose hands were intermittently wetted with a 0.5% solution of warfarin over a period of 24 days developed gross hematuria 2 days after the last contact with the solution; the following day, spontaneous hematomas appeared on the arms and legs. Within 4 days, there was also epistaxis, punctate hemorrhages of the palate and mouth, and bleeding from the lower lip. The bleeding time was over 30 minutes; the clotting time, 11 minutes, 30 seconds; prothrombin index, 17; and the prothrombin percentage (thrombotest), 5. Four days later, after treatment for 2 days with phytonadione, the values were in the normal range. Other effects of warfarin intoxication have included back pain, abdominal pain, vomiting, melena, and petechiae of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 308.3
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of warfarin): Not applicable
5. Melting point: 161 C (322 F)
6. Vapor pressure at 20 C (68 F): Data not available
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving warfarin.
4. Special precautions: None.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Warfarin is not known to be an eye irritant. It has produced hemorrhages in the retina, however, through its systemic toxicity (Grant).

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for warfarin is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with warfarin or liquids containing warfarin.
- If employees' clothing has had any possibility of being contaminated with warfarin or liquids containing warfarin, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with warfarin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of warfarin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the warfarin, the person performing the operation should be informed of warfarin's hazardous properties.
- Non-impervious clothing which becomes contaminated with warfarin should be removed promptly and not reworn until the warfarin is removed from the clothing.

SANITATION

- Skin that becomes contaminated with warfarin should be promptly washed or showered with soap or mild detergent and water to remove any warfarin.
- Eating and smoking should not be permitted in areas where warfarin or liquids containing warfarin are handled, processed, or stored.
- Employees who handle warfarin or liquids containing warfarin should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to warfarin may occur and control methods which may be effective in each case:

Operation	Controls
Application as a rodenticide	General dilution ventilation; personal protective equipment
Formulation of rodenticides	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of warfarin	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If warfarin dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If warfarin or liquids containing warfarin get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If warfarin or liquids containing warfarin penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of warfarin, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When warfarin has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If warfarin is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.

- Waste disposal methods:

Warfarin may be disposed of:

1. By making packages of warfarin in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving warfarin in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR WARFARIN

Condition	**Minimum Respiratory Protection* Required Above 0.1 mg/m^3**
Particulate Concentration	
0.5 mg/m^3 or less	Any dust respirator, except single-use.
1 mg/m^3 or less	Any dust respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Xylene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_4(CH_3)_2$
- Synonyms: Commercial xylene (xylol) is a mixture, mostly the meta-isomer. 1) O-xylene, ortho-xylene, 1,2-dimethylbenzene; 2) m-xylene, meta-xylene, 1,3-dimethylbenzene; 3) p-xylene, para-xylene, 1,4-dimethylbenzene
- Appearance and odor: Colorless liquids with aromatic odors (pure p-xylene is a solid below 12.7 C (55 F)).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for xylene is 100 parts of xylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 435 milligrams of xylene per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 100 ppm averaged over a work shift of up to ten hours per day, forty hours per week, with an acceptable ceiling level of 200 ppm averaged over a 10-minute period. The NIOSH Criteria Document for Xylene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Xylene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Xylene vapor may cause irritation of the eyes, nose, and throat. At high concentrations, xylene vapor may cause severe breathing difficulties which may be delayed in onset. At high concentrations, it may also cause dizziness, staggering, drowsiness, and unconsciousness. In addition, breathing high concentrations may cause loss of appetite, nausea, vomiting, and abdominal pain. Liquid xylene may be irritating to the eyes and skin. Exposure to high concentrations of xylene vapor may cause reversible damage to the kidneys and liver.

2. Long-term Exposure: Repeated or prolonged exposure to xylene may cause a skin rash. Repeated exposure of the eyes to high concentrations of xylene vapor may cause reversible eye damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to xylene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to xylene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, eyes, gastrointestinal tract, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Xylene has been shown to cause reversible hematopoietic depression in animals. A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Liver function tests: Since liver damage has been observed in humans exposed to xylene, a profile of liver

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has been observed in humans exposed to xylene, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on a biannual basis.

- **Summary of toxicology**

Xylene vapor irritates the eyes, mucous membranes, and skin; at high concentrations it causes narcosis. In animals, xylene causes blood changes reflecting mild toxicity to the hematopoietic system. Repeated exposure of rabbits to 1150 ppm of a mixture of isomers of xylene for 40 to 55 days caused a reversible decrease in red and white cell count and an increase in thrombocytes; exposure to 690 ppm for the same time period caused only a slight decrease in the white cell count. Three painters working in a confined space of a fuel tank were overcome by xylene vapors estimated to be 10,000 ppm; they were not found until 18.5 hours after entering the tank, and one died from pulmonary edema shortly thereafter; the other two recovered completely in 2 days; both had temporary hepatic impairment (inferred from elevated serum transaminase levels) and one of them had evidence of temporary renal impairment (increased blood urea and reduced creatinine clearance). In humans, exposure to undetermined but high concentrations caused dizziness, excitement, drowsiness, incoordination and a staggering gait. Workers exposed to concentrations above 200 ppm complain of anorexia, nausea, vomiting, and abdominal pain. Brief exposure of humans to 200 ppm caused irritation of the eyes, nose, and throat. There are reports of reversible corneal vacuolation in workers exposed to xylene, or to xylene plus other volatile solvents. The liquid is a skin irritant and causes erythema, dryness, and defatting; prolonged contact may cause the formation of vesicles.

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for xylene's three isomers: 1) ortho, 2) meta, and 3) para.

- **Physical data**

1. Molecular weight: 106.2
2. Boiling point (760 mm Hg): 1) 144.4 C (292 F); 2) 138.9 C (282 F); 3) 138.3 C (281 F)
3. Specific gravity (water = 1): 1) 0.88; 2) 0.86; 3) 0.86
4. Vapor density (air = 1 at boiling point of xylene): 3.7
5. Melting point: 1) −25 C (−12 F); 2) −48 C (−54 F); 3) 13 C (55 F)
6. Vapor pressure at 20 C (68 F): 1) 7 mm Hg; 2) 9 mm Hg; 3) 9 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1) 0.00003; 2) 0.00003; 3) 0.00003
8. Evaporation rate (butyl acetate = 1): 1) 0.7; 2) 0.7; 3) 0.7

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving xylene.
4. Special precautions: Xylene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 1) 32 C (90 F) (closed cup); 2) 28.9 C (84 F); 3) 27.2 C (81 F)
2. Autoignition temperature: 1) 465 C (869 F); 2) 530 C (986 F); 3) 530 C (986 F)
3. Flammable limits in air, % by volume: Lower: 1) 1.0; 2) 1.1; 3) 1.1; Upper: 1) 6.0; 2) 7.0; 3) 7.0
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Patty states that "the initial odor of 200 ppm has an intensity of approximately 3 and an irritation value of 1. As in most other instances, olfactory fatigue occurs rapidly and the odor is no longer detected at this concentration."
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "exposure to vapors at 200 ppm caused eye irritation in most of the persons tested. Lesions in the form of fine vacuoles in the cornea of cats exposed to commercial xylene vapors have been observed."
3. Other Information: The *Handbook of Industrial Organic Chemicals* states that xylene "may be irritating to eyes, nose and throat as exposure exceeds threshold limit." The *Hygienic Guide* notes that 200 ppm causes irritation of the nose and throat.
4. Evaluation of Warning Properties: Through its irritant effects, xylene can be detected within three times the permissible exposure limit. For the purposes of this guideline, therefore, xylene is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of xylene. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure xylene may be used. An analytical method for xylene is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid or solid xylene.
- Clothing contaminated with xylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of xylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the xylene, the person performing the operation should be informed of xylene's hazardous properties.
- Any clothing which becomes wet with liquid xylene should be removed immediately and non-impervious clothing which becomes contaminated with xylene should be removed promptly and not reworn until the xylene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid or solid xylene may contact the eyes.

SANITATION

- Skin that becomes contaminated with xylene should be promptly washed or showered with soap or mild detergent and water to remove any xylene.
- Employees who handle liquid or solid xylene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to xylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as an intermediate during manufacture of plastics, synthetic fibers, and mixed/pure isomers	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use as diluent or solvent in surface coatings, printing operations, and manufacture of rubber; degreasing agent in plastics and electronics manufacture; in organic synthesis reactions and manufacture of epoxy resins	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in formulation of insecticides	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in manufacture of xylene-formaldehyde resins; pharmaceuticals, vitamins, leather; and as a sterilizing agent for cat-gut and in microscopy	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment

Operation	Controls
Use during blending of motor and aviation fuels	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid or solid xylene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid or solid xylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid or solid xylene penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of xylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When xylene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If xylene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Xylene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of xylene vapors are permitted.
4. If the solid form, allow to melt and treat as in (3) above.

- Waste disposal method:

Xylene may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR XYLENE (XYLOL)

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Xylidine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2C_6H_3NH_2$
- Synonyms: 2,4-Dimethylaniline, etc. (6 isomers); xylidine isomers; xylidines mixed o-m-p
- Appearance and odor: Pale yellow to brown liquid with a weak, aromatic amine odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for xylidine is 5 parts of xylidine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of xylidine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for xylidine from 5 ppm to 2 ppm with a skin notation.

- Method

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Xylidine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to xylidine may affect the ability of the blood to carry oxygen normally. The earliest effect may be a bluish discoloration of the skin, especially the lips. If the lack of oxygen becomes severe, a person may have drowsiness, headache, nausea, and vomiting. If oxygen lack is very severe, it may cause unconsciousness and even death. Heart, liver, and kidney damage have occurred in animals exposed to this chemical, but have not been reported in man.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to xylidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to xylidine at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, lungs, liver, kidneys, and cardiovascular system should be stressed.

—A complete blood count: Xylidine has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin concentration in blood should be determined when xylidine intoxication is suspected.

- **Summary of toxicology**

Xylidine absorption, whether from inhalation of the vapor or absorption of the liquid through skin, causes anoxia due to the formation of methemoglobin; lung, liver, and kidney damage results in experimental animals. Repeated exposure of cats to 138 ppm caused loss of leg coordination, cyanosis, prostration, and death; at autopsy there was pulmonary edema and lobular pneumonia, necrosis of the liver, and toxic nephrosis. In cats exposed to 132 ppm for 3 days the methemoglobin concentration was 55%; repeated exposure of cats to

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17.4 ppm caused toxic hepatitis and some deaths, while repeated exposure to 7.8 ppm caused no adverse effects. Liquid xylidine penetrated the skin of rabbits in sufficient quantity to cause cyanosis and death; there were no local effects on the skin. In humans, the onset of xylidine intoxication may be insidious, in that early warning signs of methemoglobinemia such as headache and dizziness are not always interpreted as being due to overexposure, and even mild cyanosis may not be recognized.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 121.2
2. Boiling point (760 mm Hg): 212– 226 C (415–439 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of xylidine): 4.17
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with hypochlorite bleaches may form chloroamines that are explosive substances.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving xylidine.
4. Special precautions: Liquid xylidine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 96.7 C (206 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.5 (calculated at flash point)
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: May reports an odor threshold of 0.0048 ppm.
2. Eye Irritation Level: Xylidine is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of xylidine is below the permissible exposure limit, xylidine is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of xylidine in an adsorption tube containing silica gel, followed by desorption with ethanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure xylidine may be used. An analytical method for xylidine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).
(order number PB 250 159).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid xylidine.
- Clothing contaminated with xylidine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of xylidine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the xylidine, the person performing the operation should be informed of xylidine's hazardous properties.
- Where exposure of an employee's body to liquid xylidine may occur, facilities for quick drenching of the

RESPIRATORY PROTECTION FOR XYLENE (XYLOL)

Condition	**Minimum Respiratory Protection* Required Above 100 ppm**
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Xylidine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(CH_3)_2C_6H_3NH_2$
- Synonyms: 2,4-Dimethylaniline, etc. (6 isomers); xylidine isomers; xylidines mixed o-m-p
- Appearance and odor: Pale yellow to brown liquid with a weak, aromatic amine odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for xylidine is 5 parts of xylidine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of xylidine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for xylidine from 5 ppm to 2 ppm with a skin notation.

- Method

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Xylidine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to xylidine may affect the ability of the blood to carry oxygen normally. The earliest effect may be a bluish discoloration of the skin, especially the lips. If the lack of oxygen becomes severe, a person may have drowsiness, headache, nausea, and vomiting. If oxygen lack is very severe, it may cause unconsciousness and even death. Heart, liver, and kidney damage have occurred in animals exposed to this chemical, but have not been reported in man.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to xylidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to xylidine at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, lungs, liver, kidneys, and cardiovascular system should be stressed.

—A complete blood count: Xylidine has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin concentration in blood should be determined when xylidine intoxication is suspected.

- **Summary of toxicology**

Xylidine absorption, whether from inhalation of the vapor or absorption of the liquid through skin, causes anoxia due to the formation of methemoglobin; lung, liver, and kidney damage results in experimental animals. Repeated exposure of cats to 138 ppm caused loss of leg coordination, cyanosis, prostration, and death; at autopsy there was pulmonary edema and lobular pneumonia, necrosis of the liver, and toxic nephrosis. In cats exposed to 132 ppm for 3 days the methemoglobin concentration was 55%; repeated exposure of cats to

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Health Guideline for Yttrium and Compounds (as Yttrium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all yttrium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Yttrium metal

- Formula: Y
- Synonyms: None
- Appearance and odor: Odorless, silvery solid.

Yttrium nitrate hexahydrate

- Formula: $Y(NO_3)_3 \cdot 6H_2O$
- Synonyms: None
- Appearance and odor: Colorless to pink, odorless solid.

Yttrium chloride

- Formula: YCl_3
- Synonyms: None
- Appearance and odor: Colorless, odorless solid.

Yttrium oxide

- Formula: Y_2O_3
- Synonyms: None
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for yttrium and compounds is 1 milligram of yttrium and compounds (as yttrium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Animal experiments suggest that yttrium and compounds can affect the body if they are inhaled or if they come in contact with the eyes. These experiments also suggest that they can also affect the body if they are swallowed.

- **Effects of overexposure**

Long-term exposure: Yttrium chloride particles which have become embedded in the eye have caused chemical eye damage in humans. Animal studies have shown the yttrium and compounds have caused irritation of the lungs, lung damage, and liver damage.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to yttrium and compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to yttrium and compounds at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from yttrium and compounds exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of yttrium might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Yttrium may cause severe eye damage. Those with pre-existing eye problems may be at increased risk from exposure.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Yttrium and compounds have caused pulmonary irritation in animals. Systemic absorption of the citrate complex of yttrium by animals resulted in dyspnea and pulmonary edema; yttrium chloride produced liver edema, portal congestion, pleural effusion, and pulmonary hyperemia. Intraperitoneal injection of yttrium chloride in animals caused peritonitis with serous or hemorrhagic ascites. Intratracheal injection of 50 mg of yttrium oxide in rats produced diffuse sclerosis of the lungs. Application of a 0.1 M solution of yttrium chloride to the eyes of rabbits caused no injury; similar exposure of eyes from which the corneal epithelium had been removed resulted in immediate slight haziness of the cornea which subsequently became opaque and vascularized.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Yttrium metal**

1. Molecular weight: 88.9
2. Boiling point (760 mm Hg): 2927 C (5300 F)
3. Specific gravity (water = 1): 4.47
4. Vapor density (air = 1 at boiling point of yttrium metal): Not applicable
5. Melting point: 1509 C (2748 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Yttrium nitrate hexahydrate**

1. Molecular weight: 383
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 2.68
4. Vapor density (air = 1 at boiling point of yttrium nitrate hexahydrate): Not applicable
5. Melting point: 100 C (212 F) (loses water)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 142
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Yttrium chloride**

1. Molecular weight: 195.3
2. Boiling point (760 mm Hg): 1510 C (2750 F)
3. Specific gravity (water = 1): 2.67
4. Vapor density (air = 1 at boiling point of yttrium chloride): Not applicable
5. Melting point: 720 C (1328 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 79
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Yttrium oxide**

1. Molecular weight: 225.8
2. Boiling point (760 mm Hg): 4300 C (7772 F)
3. Specific gravity (water = 1): 4.84
4. Vapor density (air = 1 at boiling point of yttrium oxide): Not applicable
5. Melting point: 2416 C (4380 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of yttrium nitrate with combustible materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released when yttrium nitrate decomposes.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Not applicable

- **Warning properties**

Yttrium is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by treatment with nitric and perchloric acids, solution in hydrochloric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for yttrium and compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use dust- and splash-proof safety goggles to prevent any possibility of eye contact with yttrium nitrate hexahydrate, yttrium chloride, yttrium oxide, or liquids containing these compounds.
- Where there is any possibility that employees' eyes may be exposed to yttrium nitrate hexahydrate, yttrium chloride, yttrium oxide, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to yttrium and compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during purification; and during manufacture of alloys	Local exhaust ventilation; personal protective equipment
Use in manufacture of red phosphorus used in color TV picture tubes; fluorescent and mercury vapor lamps	Local exhaust ventilation; personal protective equipment
Use in manufacture of yttrium-iron-garnet (YIG) and YAG (aluminum) for use as electronic components in telephones, radar and space communications networks; and as simulated diamonds	Local exhaust ventilation; personal protective equipment
Use in manufacture of ceramics for use in high temperature furnaces and high intensity incandescent lamps	Local exhaust ventilation; personal protective equipment
Use in manufacture of refractories for stable, high temperature, high strength composition	Local exhaust ventilation; personal protective equipment
Use in manufacture of lasers	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If yttrium and compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If yttrium and compounds get on the skin, wash the contaminated skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of yttrium or yttrium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When yttrium and compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If yttrium and compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing yttrium and compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Yttrium and compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Yttrium as Y," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- International Labour Office: *Encyclopedia of Occupational Health and Safety,* McGraw-Hill, New York, 1971.
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RESPIRATORY PROTECTION FOR YTTRIUM AND COMPOUNDS (AS YTTRIUM)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator, except single-use.
10 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Zinc Chloride Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $ZnCl_2$
- Synonyms: None
- Appearance and odor: White fume with an acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for zinc chloride fume is 1 milligram of zinc chloride fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zinc chloride fume can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to zinc chloride fume may cause shortness of breath, a feeling of constriction in the chest, abdominal pain, watering of the eyes, burning of the eyes and throat, and coughing with phlegm and bloody sputum. It may also cause a blue color of the skin and lips. In addition, it may cause pneumonia. Breathing difficulties may not appear for several hours after exposure has ceased. Fatal exposures have occurred.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to zinc chloride fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to zinc chloride fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Zinc chloride fume causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Zinc chloride fume is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing. Determination of zinc in the urine may be helpful in evaluating the extent of absorption.

- **Summary of toxicology**

Zinc chloride fume irritates the eyes, mucous membranes, and skin, and causes delayed pulmonary edema. Ten deaths and 25 cases of non-fatal injury occurred among 70 persons exposed to a high concentration of zinc chloride released from smoke generators; presenting symptoms were conjunctivitis (two with burns of the corneas), irritation of nose and throat, cough with copious sputum, dyspnea, constrictive sensation in the chest, stridor, retrosternal pain, nausea, epigastric pain, and pale gray cyanosis. Of the 10 fatalities, a few died immediately or in a few hours from pulmonary edema, while those who survived longer developed bronchopneumonia. Between the second and fourth days after exposure, almost all cases developed moist, adventitious sounds in the lungs, and the majority continued to

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present a pale cyanotic color; a prominent feature was the disparity between the severe symptoms and the paucity of physical signs in the lungs; recovery occurred within 1 to 6 weeks after the incident. A firefighter was fatally exposed to a high but undetermined concentration of zinc chloride fume from a smoke generator; on admission to the hospital, the patient complained of nausea, sore throat, and chest tightness aggravated by deep inspiration. He initially improved but then developed tachypnea, substernal soreness, fever, cyanosis, and coma; the lung fields were clear on auscultation despite diffuse pulmonary infiltrations seen on the chest roentgenogram; death occurred 18 days after exposure, and autopsy revealed active fibroblastic proliferation and cor pulmonale. Injection of zinc chloride solution into the testes of 49 Syrian hamsters resulted in areas of necrosis occupying about 25% of each testis; two embryonal carcinomata of the testis were found 10 weeks later at necropsy.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 136.3
  2. Boiling point (760 mm Hg): 732 C (1350 F) (for solid)
  3. Specific gravity (water = 1): 2.91 (solid)
  4. Vapor density (air = 1 at boiling point of zinc chloride fume): Not applicable
  5. Melting point: 283 C (541 F) (for solid)
  6. Vapor pressure at 20 C (68 F): Not applicable
  7. Solubility in water, g/100 g water at 25 C (77 F): 81
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant states that "dilute solutions (0.2% to 1%) have long been used as astringent eye drops without difficulty, but concentrated solutions and pastes such as encountered industrially have caused very severe injuries of the cornea in numerous cases of accidental splash in the eye. . . . Guillery found that applying 10% zinc chloride solution for 4 to 5 minutes to a rabbit's eye caused loss of corneal endothelium and extensive infiltration." No information is available concerning the effects on the eye specifically of the fume of zinc chloride.

The *Documentation of TLV's* reports, "Elkins stated that zinc chloride is an irritant . . . . Ferry, in investigating a borderline condition, found that levels between 0.07 and 0.4 mg/m^3 for 30 minutes did not result in sensory effects. The fume is corrosive to metals at these levels, however."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for zinc chloride fume had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to zinc chloride fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fluxing iron/steel prior to galvanizing	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from arc welding of galvanized iron and steel pipes	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from fluxing agent in some solder composition	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from vulcanizing and reclaiming processes for rubber	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from solutions in glass and metal etching	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from manufacture of dry cell batteries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from petroleum refining operations	Process enclosure; general dilution ventilation; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of zinc chloride fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of zinc chloride fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Zinc Chloride Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR ZINC CHLORIDE FUME

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
10 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Zinc Oxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ZnO
- Synonyms: None
- Appearance: White fume.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for zinc oxide fume is 5 milligrams of zinc oxide fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to 5 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 15 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Zinc Oxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zinc oxide fume can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Zinc oxide fume causes a flu-like illness called metal fume fever. Symptoms of metal fume fever include headache, fever, chills, muscle aches, nausea, vomiting, weakness, and tiredness. The symptoms usually start several hours after exposure. The attack may last 6 to 24 hours. Metal fume fever is more likely to occur after a period away from the job (after weekends or vacations). High levels of exposure to zinc oxide fume may cause a metallic or sweet taste in the mouth, dryness and irritation of the throat, and coughing at the time of exposure.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to zinc oxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to zinc oxide fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Zinc oxide fume may cause respiratory impairment. Persons with pulmonary disease may be more susceptible to the effect os zinc oxide fume. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Persons with pre-existing pulmonary disease may be more susceptible to the effects of zinc oxide fume. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing. Determination of zinc in the urine may be helpful in evaluating the extent of absorption.

- **Summary of toxicology**

Inhalation of zinc oxide fume causes an influenza-like illness termed metal fume fever. Heavy human exposure to zinc oxide fume may cause an immediate dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness and constriction in the chest, and a dry cough. Several hours following exposure the subject develops fever, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Physical examination reveals fever, eventually followed by perspiration and chills, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity; there is usually leukocytosis, which may amount to 12,000 to 16,000/MM3. An attack usually subsides after 6 to 12 hours but may last for up to 24 hours; recovery is usually complete. Most workers rapidly develop an immunity to these attacks, but it is as quickly lost; attacks tend to be more severe on the first day of the work-week. Only freshly formed fume causes the illness, presumably because flocculation occurs in the air; the larger particles that form are deposited in the upper respiratory tract and do not penetrate deeply into the lungs. Chills have been reported in workers from exposure to concentrations of zinc oxide fume below 5 mg/m^3.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 81.37
  2. Boiling point (760 mm Hg): Solid sublimes
  3. Specific gravity (water = 1): 5.6 (solid)
  4. Vapor density (air = 1 at boiling point of zinc oxide fume): Not applicable
  5. Melting point: Greater than 1800 C (greater than 3272 F)
  6. Vapor pressure at 20 C (68 F): Not applicable
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble (solid)
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Zinc oxide fume may react violently with chlorinated rubber.
  3. Hazardous decomposiiton products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Zinc oxide fume is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of zinc oxide fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of zinc oxide on a cellulose membrane filter, followed by solublizing the zinc with nitric acid and analyzing by atomic absorption spectrophotometry. An analytical method for zinc oxide fume is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to zinc oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during brazing, welding, burning, and cutting of zinc and galvanized metals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from founding of brass, copper, and zinc, and galvanizing of iron and steel	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from abrasive cleaning of galvanized metal surface	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberating during use as a ceramic flux	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during recovery of impure lead blast furnace slag; from manufacture of glass to increase brilliance and luster of glass	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from use as an intermediate in manufacture of other zinc compounds; in manufacture of electronic devices	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from use as a filler material in crushed stone industry	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of zinc oxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of zinc oxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Zinc Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR ZINC OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2,500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 2,500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Zirconium Compounds (as Zirconium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all zirconium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Zirconium oxide

- Formula: ZrO_2
- Synonyms: Zirconia
- Appearance and odor: Colorless, odorless solid.

Zirconium oxychloride

- Formula: $ZrOCl_2\,8H_2O$
- Synonyms: Zirconyl chloride octahydrate
- Appearance and odor: Colorless, odorless solid.

Zirconium tetrachloride

- Formula: $ZrCl_4$
- Synonyms: ZC-4
- Appearance and odor: Colorless solid with an acrid odor in moist air.

Zirconium hydride

- Formula: ZrH_2
- Synonyms: Zirconium dihydride
- Appearance and odor: Odorless, metallic powder.

Zirconyl acetate

- Formula: $H_2ZrO_2(C_2H_3O_2)_2$
- Synonyms: Diacetatozirconic acid
- Appearance: Colorless solid.
- **Summary of toxicology**

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for zirconium compounds is 5 milligrams of zirconium compounds (as zirconium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zirconium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

Skin rash has been reported from exposure to zirconium-containing deodorants.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to zirconium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to zirconium compounds at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from zirconium compounds exposure.

—Chronic respiratory disease: Zirconium compounds (silicate) have been reported to cause radiographic changes in animals due to pulmonary retention. Zirconium hexachloride may be irritating to the mucous membranes of the respiratory tract.

—Skin disease: Zirconium may cause granulomas of the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

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2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Zirconium compounds are of generally low toxicity, although granulomata have been produced by repeated topical applications of zirconium salts to human skin. In rats, the oral LD50 of several zirconium compounds ranged from 2.5 to 10 g/kg. Repeated inhalation of zirconium tetrachloride mist by dogs for 2 months at 6 mg/m^3 as zirconium caused slight decreases in hemoglobin and in erythrocyte counts, with some increases in mortality over that of controls; these effects may have been due to the liberation of hydrogen chloride. However, animals exposed to zirconium dioxide dust for 1 month at 75 mg/m^3 as zirconium showed no detectable effects. Rats exposed to high concentrations of zirconium silicate dust for 7 months developed radiographic shadows in the lungs; these were attributed solely to the deposition of the radiopaque particles, since histologic examination showed no cellular reaction. A study of 22 workers exposed to fumes from a zirconium reduction process for 1 to 5 years revealed no abnormalities referable to the exposure. There are no well-documented cases of toxic effects from industrial exposure. Granulomata of the human axillary skin have occurred from use of deodorants containing zirconium, although the metal is not regarded as a skin sensitizer in other types of exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Zirconium oxide**

1. Molecular weight: 123.2
2. Boiling point (760 mm Hg): 5000 C (9032 F)
3. Specific gravity (water = 1): 5.8 to 6.2
4. Vapor density (air = 1 at boiling point of zirconium oxide): Not applicable
5. Melting point: 2700 C (4892 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Zirconium oxychloride**

1. Molecular weight: 322.3
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of zirconium oxychloride): Not applicable
5. Melting point: 110 C (230 F) (approximately)
6. Vapor pressure at 20 C (68 F): 9 to 13 mm Hg vapor pressure of water
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Zirconium tetrachloride**

1. Molecular weight: 233
2. Boiling point (760 mm Hg): 331 C (628 F) (sublimes)
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of zirconium tetrachloride): Not applicable
5. Melting point: 331 C (628 F) (sublimes)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Zirconium hydride**

1. Molecular weight: 93.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 5.7
4. Vapor density (air = 1 at boiling point of zirconium hydride): Not applicable
5. Melting point: Decomposes above 300 C (572 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Very low
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Zirconyl acetate**

1. Molecular weight: Very high (a polymer)
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of zirconyl acetate): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Zirconium tetrachloride will decompose in the presence of moist air. Elevated temperatures (greater than 315 C (600 F)) cause zirconium hydride to decompose to give off flammable hydrogen gas.
2. Incompatibilities: Zirconium tetrachloride reacts with water or with moisture in air to form hydrochloric acid fume. Contact with alkali metals such as sodium or potassium may cause explosions. Contact of zirconium hydride with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving zirconium compounds.
4. Special precautions: Zirconium tetrachloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For zirconium hydride: 270 C (518 F); for others: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For zirconium hydride, sand or

inert powder; for others, not applicable

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of zirconium compounds on a filter, followed by treatment with nitric and perchloric acids, solution in acid, and atomic absorption spectrophotometric analysis. An analytical method for zirconium compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, and Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with zirconium oxide, zirconium oxychloride, zirconyl acetate, or liquids containing these compounds, and to prevent skin contact with zirconium tetrachloride or liquids containing zirconium tetrachloride, where skin contact may occur.
- If employees' clothing may have become contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where exposure of an employee's body to zirconium tetrachloride or liquids containing zirconium tetrachloride may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate or zirconium tetrachloride should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of zirconium tetrachloride or liquids containing zirconium tetrachloride contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to zirconium tetrachloride or liquids containing zirconium tetrachloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

containing zirconium tetrachloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.
- Employees who handle zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride, or liquids containing these compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to zirconium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from refining and casting operations, dies for metal extrusion and spout linings for continuous casting; during preparation of alloys; during manufacture of metal or alloys in nuclear power, aerospace, and chemical industries	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of ceramics, glass, and porcelains; synthesis of pigments, dyes, and water repellants; use in tanning operations	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as abrasive and polishing materials; use as an igniter in manufacture of munitions and other items as detonators, photoflash bulbs, and lighter flints; use in manufacture of skin ointments and antiperspirants	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a gas getter in manufacture of high vacuum tubes and radio valves; use as a deoxidizer, denitrifier, and desulfurizer in iron and steel manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation from chemical synthesis	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If zirconium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If zirconium compounds get on the skin, wash with soap or mild detergent and water.

- **Breathing**

If a person breathes in large amounts of zirconium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When zirconium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If zirconium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing zirconium oxide, zirconium oxychloride, zirconium tetrachloride, zirconium hydride, or zirconyl acetate should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Zirconium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ZIRCONIUM COMPOUNDS (AS ZIRCONIUM)

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
25 mg/m³ or less	Any dust and mist respirator, except single-use.
50 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

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