Occupational Health Guideline for Dioxane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: OCH₃CH₂OCH₂CH₂
- Synonyms: Diethylene dioxide; diethylene ether; dioxan; p-dioxane; 1,4-dioxane
- Appearance and odor: Colorless liquid with a mild ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dioxane is 100 parts of dioxane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of dioxane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 1 ppm averaged over a 30-minute period, and that dioxane be regulated as an occupational carcinogen. The NIOSH Criteria Document for Dioxane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- Routes of exposure
  Dioxane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.
- Effects of overexposure
  Overexposure to dioxane may cause irritation of the eyes, nose, and throat. It may also cause drowsiness, dizziness, loss of appetite, headache, nausea, vomiting, stomach pain, and liver and kidney damage. Prolonged skin exposure to the liquid may cause drying and cracking. Dioxane has been shown to induce tumor formation in experimental animals.
- Reporting signs and symptoms
  A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dioxane.
- Recommended medical surveillance
  The following medical procedures should be made available to each employee who is exposed to dioxane at potentially hazardous levels:
  1. *Initial Medical Examination:*
     - A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the upper respiratory system, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.
     - Liver function tests: Dioxane may cause liver damage. A profile of liver function should be performed by using a medically acceptable array of biochemical tests.
     - Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.
     - Skin disease: Dioxane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.
     - 14" x 17" chest roentgenogram: Dioxane causes human lung damage. Surveillance of the lungs is indicated.
  2. *Periodic Medical Examination:*
     - The aforementioned medical examinations should be repeated on an annual basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service  Center for Disease Control
National Institute for Occupational Safety and Health

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

September 1978
• Summary of toxicology
Dioxane vapor is a mucous membrane irritant, and on prolonged exposure is toxic to the liver and kidneys. Repeated exposure of several animal species to 1000 ppm produced damage to kidneys and liver, and the repeated inhalation of 800 ppm over 30 days resulted in fatal kidney injury in some rabbits. Human volunteers exposed for 15 minutes to 300 ppm reported mild transient irritation of the eyes, nose, and throat. There is significant absorption of the liquid through the skin, adding to the inhalation hazard. Prolonged or repeated skin contact may also result in drying and cracking due to defatting action. Fatal intoxication due to liver necrosis and severe kidney damage has been reported in workers after two months of heavy exposure to dioxane vapor; the onset of poisoning was marked by drowsiness and headache, nausea, vomiting, and irritation of the eyes and respiratory passages. In one fatal case there was significant damage to the brain as well as to liver and kidney. Due to its mild odor, serious or fatal exposures have been experienced without forewarning. Tumors of the nose, liver, and lungs have been reported in animals following ingestion of high concentrations of dioxane. Immersion of chick embryos in dioxane has been reported to cause possible mutagenic effects. The significance of these findings in humans is unknown.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data
1. Molecular weight: 88
2. Boiling point (760 mm Hg): 101°C (214°F)
3. Specific gravity (water = 1): 1.03
4. Vapor density (air = 1 at boiling point of dioxane): 3.0
5. Melting point: 11.8°C (53°F)
6. Vapor pressure at 20°C (68°F): 29 mm Hg
7. Solubility in water, g/100 g water at 20°C (68°F):
Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 2.7

• Reactivity
1. Conditions contributing to instability: Heat, long exposure to moisture.
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dioxane.
4. Special precautions: Dioxane is hydroscopic and will produce peroxides in the presence of moisture. Dioxane containing peroxides should not be distilled to dryness because of the potential explosion of non-volatile peroxides.

• Flammability
1. Flash point: 12°C (54°F) (closed cup)
2. Autoignition temperature: 180°C (356°F)
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 22.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• Warning properties
1. Odor Threshold: Summer reports an odor threshold of 170 ppm; May reports 2.7 and 170 ppm.
2. Eye Irritation Level: Grant states that “in human beings, irritation of the eye is noted only at concentrations greater than 220 ppm of vapor in air.” Patty states that at 300 ppm, dioxane “caused irritation of the eyes, nose, and throat; and at 500 ppm, it was objectionable. Even at higher concentrations, the initial irritation to eyes and respiratory passages is transitory . . . .”
3. Evaluation of Warning Properties: Patty states that the initial irritation produced by exposure to dioxane is transitory and that the “warning properties of dioxane are completely inadequate to prevent exposure to toxic amounts.” The AIHA Hygienic Guide also notes that “the vapor has poor warning properties and can be inhaled in amounts which may cause serious intoxication or death with injury of the liver and kidneys.”

MONITORING AND MEASUREMENT PROCEDURES

• General
Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method
Sampling and analyses may be performed by collection of dioxane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dioxane may be used. An analytical method for dioxane is in the NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted
are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid dioxane.
- Any clothing which becomes wet with liquid dioxane should be removed immediately and non-impervious clothing which becomes contaminated with dioxane should be removed promptly and such clothing should not be re-worn until the dioxane is removed from the clothing.
- Clothing wet with liquid dioxane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dioxane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dioxane, the person performing the operation should be informed of dioxane’s hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dioxane may contact the eyes.

SANITATION

- Skin that becomes contaminated with dioxane should be promptly washed or showered to remove any dioxane.
- Eating and smoking should not be permitted in areas where liquid dioxane is handled, processed, or stored.
- Employees who handle liquid dioxane should wash their hands thoroughly before eating, smoking, or using toilet facilities.
- Areas in which exposure to dioxane may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dioxane may occur and control methods which may be effective in each case:

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
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<tbody>
<tr>
<td>Use in spray application of natural and synthetic resin-based varnishes, lacquers, and paints</td>
<td>Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use in dipping, roller coating, tumbling, knitting, and brushing of natural and synthetic resin-based varnishes, lacquers, and paints</td>
<td>Local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use as a solvent for fats, oils, waxes, greases, and natural and synthetic resins</td>
<td>Local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
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<tr>
<td>Use as a wetting agent in textile processing, dye baths, and stain and printing compositions</td>
<td>Local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
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<tr>
<td>Use as a degreaser</td>
<td>Local exhaust ventilation</td>
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<tr>
<td>Use as a dehydrating agent in preparation of histological slides</td>
<td>Local exhaust ventilation</td>
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<tr>
<td>Use in manufacture of detergents and cleaning preparations; manufacture of polishing compounds</td>
<td>Local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
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<tr>
<td>Use as a stabilizer for chlorinated solvents; use in preparation of cosmetics and deodorants; use in purification of drugs</td>
<td>Local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
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<tr>
<td>Use as a working fluid for scintillation counter samples</td>
<td>General dilution ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use as a solvent in pulping of wood; polishing compounds</td>
<td>Local exhaust ventilation; general dilution ventilation; personal protective equipment</td>
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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**
  If dioxane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**
  If dioxane gets on the skin, promptly wash the contaminated skin with water. If dioxane soaks through the clothing, remove the clothing promptly and wash the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**
  If a person breathes in large amounts of dioxane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**
  When dioxane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**
  Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility’s emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If dioxane is spilled or leaked, the following steps should be taken:
  1. Remove all ignition sources.
  2. Ventilate area of spill or leak.
  3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Dioxane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:
  Dioxane may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES


* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man. Volume 11, 1976.
# RESPIRATORY PROTECTION FOR DIOXANE

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 100 ppm</th>
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<tr>
<td><strong>Vapor Concentration</strong></td>
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<tr>
<td>200 ppm or less</td>
<td>Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.</td>
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</tbody>
</table>
| Greater than 200 ppm or entry and escape from unknown concentrations | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  
A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode. |
| **Fire Fighting**                        | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. |
| **Escape**                               | Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus. |

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