

Occupational Health Guideline for Crotonaldehyde

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: $\text{CH}_3\text{CH}=\text{CHCHO}$
- Synonyms: Beta-methylacrolein; propylene aldehyde; crotonic aldehyde; 2-butenal
- Appearance and odor: Colorless to straw-colored liquid with an irritating, pungent, and suffocating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for crotonaldehyde is 2 parts of crotonaldehyde per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of crotonaldehyde per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- Routes of exposure
Crotonaldehyde can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.
- Effects of overexposure
 1. *Short-term Exposure:* Crotonaldehyde causes irritation of the eyes, nose, and throat. It may also cause an irritation of the skin and difficulty in breathing which may occur several hours after exposure.
 2. *Long-term Exposure:* None known
 3. *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 crotonaldehyde.

- Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to crotonaldehyde at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from crotonaldehyde exposure.

—Chronic respiratory disease: Crotonaldehyde causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of crotonaldehyde might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Crotonaldehyde is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- Summary of toxicology

Crotonaldehyde vapor irritates the eyes and respiratory tract. Rats did not survive exposure to 1650 ppm for 10 minutes; there was respiratory distress, an excitatory stage, and terminal convulsions; autopsy revealed bronchiolar damage. Pulmonary edema has also been observed in rats dead of exposure to 1500 ppm for 30 minutes. Human subjects exposed to 45 ppm for a few seconds experienced conjunctival irritation; at 15 ppm there was no eye discomfort. The liquid when placed in the eyes of rabbits caused severe injury. In a series of eight cases of corneal injury from industrial exposure to crotonaldehyde, healing was complete in 48 hours; the severity of exposure was not specified. A case of apparent sensitization of undetermined nature to crotonaldehyde has been reported in a laboratory worker.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data

1. Molecular weight: 70.1

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 Centers for Disease Control
National Institute for Occupational Safety and Health

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

2. Boiling point (760 mm Hg): 102 C (216 F)
3. Specific gravity (water = 1): 0.85
4. Vapor density (air = 1 at boiling point of crotonaldehyde): 2.4
5. Melting point: -75 C (-103 F)
6. Vapor pressure at 20 C (68 F): 30 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 15.5

8. Evaporation rate (butyl acetate = 1): 2.7

• **Reactivity**

1. Conditions contributing to instability: Heat may cause polymerization to occur and containers to burst.

2. Incompatibilities: Contact with caustics, ammonia, organic amines, and mineral acids may cause violent polymerization to occur. Contact with strong oxidizers may cause fires and explosions. Crotonaldehyde is readily converted by oxygen to peroxides and acids.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving crotonaldehyde.

4. Special precautions: Liquid crotonaldehyde will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 12.8 C (55 F) (closed cup)

2. Autoignition temperature: 232 C (450 F)

3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 15.5

4. Extinguishant: Carbon dioxide, dry chemical, alcohol foam

• **Warning properties**

1. Odor Threshold: Stern and May report odor thresholds for crotonaldehyde of 0.062 and 0.035 ppm, respectively.

2. Eye Irritation Level: Both Grant and the *Documentation of TLV's* report that "humans have experienced "considerable eye discomfort" at 45 ppm for a brief exposure (a few seconds). Humans did not experience eye irritation during an exposure of a few seconds to 15 ppm. The threshold of eye irritation is not given, however.

3. Other Information: According to the *Documentation of TLV's*, crotonaldehyde is also a respiratory tract irritant. The threshold limit was recommended "to prevent irritation of eyes and respiratory passages."

4. Evaluation of Warning Properties: Since the odor threshold of crotonaldehyde is below the permissible exposure limit, it is treated as a material with adequate warning properties.

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**

An analytical method for crotonaldehyde 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 skin contact with liquid crotonaldehyde or liquids containing crotonaldehyde, where skin contact may occur.

• Clothing wet with liquid crotonaldehyde or liquids containing crotonaldehyde should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of crotonaldehyde from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the crotonaldehyde, the person performing the operation should be informed of crotonaldehyde's hazardous properties.

• Where exposure of an employee's body to liquid crotonaldehyde or liquids containing crotonaldehyde may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes wet with and non-impervious clothing which becomes contaminated with crotonaldehyde should be removed immediately and not re worn until the crotonaldehyde is removed from the clothing.

• Employees should be provided with and required to

use splash-proof safety goggles where there is any possibility of liquid crotonaldehyde or liquids containing crotonaldehyde contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquid crotonaldehyde or liquids containing more than 1% of crotonaldehyde by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with crotonaldehyde should be immediately washed or showered to remove any crotonaldehyde.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use an intermediate in manufacture of butyl alcohol; use in polymer technology as a reaction medium, formulator, adhesive, antioxidant, corrosion inhibitor, and stabilizer	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis in manufacture of dyestuffs, sedatives, pesticides, and flavoring agents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for purification of mineral and lubricating oils; use during manufacture of surface active agents as bactericides for petroleum well fluids, metal brighteners, and leather/paper sizing materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture as warning agent in fuel gases for locating breaks and leaks in pipes; use in leather tanning and preparation of tanning materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation

Use in manufacture of rubber and rubber antioxidants and accelerators; use in manufacture of chemical warfare agents; use in photographic emulsion as a hardening agent for gelatin

Controls

Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

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 liquid crotonaldehyde or liquids containing crotonaldehyde get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid crotonaldehyde or liquids containing crotonaldehyde get on the skin, immediately flush the contaminated skin with water. If liquid crotonaldehyde or liquids containing crotonaldehyde soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of crotonaldehyde, 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 crotonaldehyde has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• 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 crotonaldehyde or liquids containing crotonaldehyde are 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 reclaimed or collected and atomized in a suitable combustion chamber. Liquid crotonaldehyde should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of crotonaldehyde vapors are permitted.

- Waste disposal method:

Crotonaldehyde may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Crotonaldehyde (beta-Methyl Acrolein)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products*

(3rd ed.), Williams and Wilkins, Baltimore, 1969.

- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

- Henson, E. V.: "The Toxicology of Some Aliphatic Aldehydes," *Journal of Occupational Medicine*, pp. 457-461, August 1959.

- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.

- May, J.: "Solvent Odor Thresholds for the Evaluation of Solvent Odors in the Atmosphere," *Staub-Reinhalt*, 26:9, 385-389, 1966.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

- Rinehart, W. E.: "The Effect on Rats of Single Exposures to Crotonaldehyde Vapor," *American Industrial Hygiene Association Journal*, 28:561-566, 1967.

- Smyth, H. F., and Carpenter, C. P.: "Chemical Burns of the Rabbit Cornea," *American Journal of Ophthalmology*, 29:1363-72, 1946.

- Smyth, H. F., and Carpenter, C. P.: "The Place of the Range-Finding Test in the Industrial Toxicology Laboratory," *Journal of Industrial Hygiene and Toxicology*, 26:8, pp. 269-73, 1944.

- Smyth, H. F., et al.: "Range-Finding Toxicity Data, List III," *Journal of Industrial Hygiene and Toxicology*, 31:1, pp. 60-62, 1949.

- Stern, A. C. (ed.): *Air Pollution* (2nd ed.), Academic Press, New York, 1968.

- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Chemical Company Guide - Crotonaldehyde*, New York, 1967.

RESPIRATORY PROTECTION FOR CROTONALDEHYDE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Vapor Concentration	
100 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
400 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 400 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.

