OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 1,3-DICHLOROPROPENE

INTRODUCTION

This guideline summarizes pertinent information about 1,3-dichloropropene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

Formula

C₃H₄Cl₂

• Structure

$$CI \longrightarrow C = C \xrightarrow{CH_2CI} CI \longrightarrow C = C \xrightarrow{H} CH_2CI$$

• Synonyms

alpha-Chloroallyl chloride; gamma-chloroallyl chloride; 1,3-dichloropropylene; 1,3-dichloropropene-1; Telone; Telone II; Dorlone; alpha,gamma-dichloropropylene.

Identifiers

1. CAS No.: 542-75-6

2. RTECS No.: UC8310000

3. DOT UN: 2047 29

4. DOT label: Flammable liquid

· Appearance and odor

1,3-Dichloropropene is a straw-colored liquid with a chloroform-like odor; the commercial product consists of the cis- and trans-isomers in approximately equal parts.

CHEMICAL AND PHYSICAL PROPERTIES

· Physical data

1. Molecular weight: 110.98

2. Boiling point (760 mm Hg): 103°C (217°F)

3. Specific gravity (water = 1): 1.2 at 20°C (68°F)

4. Vapor density at 37.8°C (100°F): 3.8

5. Freezing point: -84°C (-119.2°F)

6. Vapor pressure at 25°C (77°F): approximately 28 mm Hg

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- Solubility: Insoluble in water; soluble in acetone, toluene, octane, carbon tetrachloride, n-heptane, methanol, and benzene.
- 8. Evaporation rate: Data not available

Reactivity

- Conditions contributing to instability: Heat, sparks, and open flame. The vapors of this substance also form explosive mixtures with air.
- Incompatibilities: Contact of 1,3-dichloropropene with oxidizers, aluminum or magnesium compounds, or alkaline or corrosive materials causes a violent reaction.
- 3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 1,3-dichloropropene.
- Special precautions: This substance can polymerize if not stabilized with epichlorohydrin or another stabilizer.

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to 1,3-dichloropropene.

- 1. Flash point: 35°C (95°F) (open cup)
- 2. Autoignition temperature: Data not available
- 3. Flammable limits in air (% by volume): Lower, 5.3; upper, 14.5
- 4. Extinguishant: Use water spray, dry chemical, standard foam, or carbon dioxide to fight fires involving 1,3-dichloropropene. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving 1,3-dichloropropene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of 1,3-dichloropropene may explode in the heat of the fire and should be moved from

the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container is discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 1,3-dichloropropene. Structural firefighters' protective clothing may provide limited protection against fires involving 1,3-dichloropropene.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 1,3-dichloropropene [29 CFR 1910.1000, Table Z-11.

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (5 mg/m³) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure. However, 1,3-dichloropropene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 1,3-dichloropropene a threshold limit value (TLV) of 1 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 1,3-dichloropropene [ACGIH 1991].

· Rationale for limits

The NIOSH limit is based on the potential for cancer associated with 1,3-dichloropropene exposure. The ACGIH limit is based on the risk of kidney injury associated with exposure to 1,3-dichloropropene.

HEALTH HAZARD INFORMATION

· Routes of exposure

Exposure to 1,3-dichloropropene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

Summary of toxicology

1. Effects on Animals: Exposure to 1,3-dichloropropene irritates the skin, eyes, and mucous membranes and may cause respiratory tract, liver, and kidney damage in experimental animals. 1,3-Dichloropropene is also carcinogenic in rodents. Exposure to 1,3-dichloropropene vapor (concentration and duration not specified) caused moderate to severe conjunctival irritation and slight to moderate reversible corneal injury in rabbits; applied to the skin of animals of the same species, this substance caused swelling and necrosis [Clayton and Clayton 1981]. The dermal LD₅₀ in rabbits for the same solution is 504 mg/kg [ACGIH 1991]. The LC_{so} in rats is 500 ppm for an unspecified period of time, while the 2-hr LC₅₀ in mice is 1,033 ppm [NIOSH 1993]. The oral LD₅₀ for a 10-percent solution of 1,3-dichloropropene (92-percent purity) in corn oil is 713 mg/kg in male rats and 470 mg/kg in female rats [ACGIH 1991]. Acute inhalation exposure (duration not specified) to concentrations above 2,700 ppm irritated the eyes and nose and caused serious injury to the lungs, liver, and kidneys of rats; exposure to a 1,000 ppm concentration for a period described as "brief" caused severe eye irritation and loss of consciousness, while exposure to 1,000 ppm for 2 hours was lethal to all exposed rats [ACGIH 1991]. Exposure to a 3 ppm concentration of 1,3dichloropropene for 7-hours a day, 5 days a week for 6 months produced reversible swelling of renal tubular epithelium in rats [ACGIH 1991]. Rats and mice exposed to 0, 93, 32, or 12 ppm for 7 hours a day, 5 days a week for 13 weeks experienced growth depression (high dose rats and female mice) and focal changes of the nasal epithelium in high dose rats (both sexes) and female rats exposed to 32 ppm [Clayton and Clayton 1981]. 1,3-Dichloropropene has been tested in oral carcinogenicity bioassays in both mice and rats. In mice, it produced dose-related increases in the incidences of benign and/or malignant tumors of the urinary bladder, lung, and forestomach. In male rats, it caused dose-related increases in the incidences of benign and malignant forestomach tumors and benign liver tumors; in female rats, it produced benign forestomach tumors

[IARC 1986]. Based on this evidence, the International Agency for Research on Cancer has concluded that the evidence for the carcinogenicity of technical-grade 1,3-dichloropropene in animals is sufficient [IARC 1986].

2. Effects on Humans: Exposure to 1,3-dichloropropene irritates the eyes, skin, and mucous membranes and may produce respiratory damage in humans. Prolonged skin contact with this substance may cause burns or an itching, red rash [NLM 1992]. After an explosion of a tank car containing this substance, exposed workers immediately experienced coughing and choking, followed by headache, dizziness, irritation of the mucous membranes, and chest discomfort; three of the exposed workers lost consciousness and subsequently died. Pulmonary effects included atelectasis, emphysema, pneumonia, and pulmonary edema [Gosselin et al. 1984]. Individuals exposed to 1,3-dichloropropene during a spill reported headache, fatigue, irritation of the mucous membranes, chest pain, and abdominal discomfort that persisted for up to 2 weeks [Gosselin et al. 1984]. Two firemen previously treated for acute symptoms after exposure to 1,3-dichloropropene subsequently developed malignant histiocytic lymphomas [IARC 1986].

· Signs and symptoms of exposure

- Acute exposure: The signs and symptoms of acute exposure to 1,3-dichloropropene include pain, redness, and tearing of the eyes; redness and inflammation of the eyelids; redness, burns, and rashes of the skin; headache; fatigue; loss of consciousness; coughing; shortness of breath; chest discomfort; abdominal discomfort; and vomiting. In addition, two cases of malignant histiocytic lymphoma have been reported in workers acutely overexposed to this substance.
- 2. Chronic exposure: The signs and symptoms of chronic exposure to 1,3-dichloropropene include skin burns and cracked, rough, and reddened skin.

• Emergency procedures

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

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

- 1. Eye exposure: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of 1,3-dichloropropene! Immediately but gently flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! Immediately, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.
- 3. Inhalation exposure: Move the victim to fresh air immediately.

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

- 4. Ingestion exposure: Take the following steps if 1,3-dichloropropene or any material containing it is ingested:
 - -Do not induce vomiting.
 - —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and no more.
 - —Do not permit the victim to drink milk or carbonated beverages!
 - —Do not permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

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

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

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 1,3-dichloropropene and lead to worker exposures to this substance:

- -Use as a soil fumigant
- -Use as a chemical intermediate

The following methods are effective in controlling worker exposures to 1,3-dichloropropene, depending on the feasibility of implementation:

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

Good sources of information on control methods are as follows:

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

MEDICAL MONITORING

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

· Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to 1,3-dichloropropene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 1,3-dichloropropene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 1,3-dichloropropene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 1,3-dichloropropene on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 1,3-dichloropropene.

Medical examinations recommended at the time of job transfer or termination

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

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 1,3-dichloropropene is made using a charcoal solid sorbent tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 5 liters is collected. The sample is then treated with carbon disulfide to extract the 1,3-dichloropropene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in NIOSH Method No. 1003 in the NIOSH Analytical Methods Manual [NIOSH 1984], which has been modified for use by OSHA.

PERSONAL HYGIENE

1,3-Dichloropropene can be absorbed through the skin in toxic amounts. Therefore, if 1,3-dichloropropene contacts

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

Clothing contaminated with 1,3-dichloropropene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of 1,3-dichloropropene, particularly its ability to be absorbed through the skin in toxic amounts.

A worker who handles 1,3-dichloropropene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 1,3-dichloropropene is handled, processed, or stored.

STORAGE

1,3-Dichloropropene should be stored in a cool, dry, wellventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Electrical equipment in storage areas must meet requirements for OSHA Class I flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of 1,3-dichloropropene should be protected from physical damage and should be stored separately from oxidizers, aluminum or magnesium compounds, alkaline or corrosive materials, and heat, sparks. and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle 1,3dichloropropene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained 1,3-dichloropropene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 1,3-dichloropropene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

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

- 2. Notify safety personnel.
- 3. Remove all sources of heat and ignition.
- 4. Ventilate potentially explosive atmospheres.
- Use water spray to reduce vapors; do not get water inside the container.
- For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
- For large liquid spills, build dikes far ahead of the spill to contain the 1,3-dichloropropene for later reclamation or disposal.

SPECIAL REQUIREMENTS

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

• Emergency planning requirements

1,3-Dichloropropene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

Reportable quantity requirements for hazardous releases

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

The reportable quantity for 1,3-dichloropropene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employers are required to do the following:

-Notify the National Response Center immediately at

(202) 426-2675 or at (800) 424-8802 in Washington, D.C. [40 CFR 302.6].

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

· Community right-to-know requirements

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of 1,3-dichloropropene per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 1,3-dichloropropene emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. 1,3-Dichloropropene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U084. This chemical is approved for land disposal as long as the concentration of 1,3-dichloropropene in the waste or treatment residual does not exceed 18 mg/kg. 1,3-Dichloropropene also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

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

RESPIRATORY PROTECTION

· Conditions for respirator use

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

Respiratory protection program

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

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with 1,3-dichloropropene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by 1,3-dichloropropene and may provide protection for periods greater than 8 hours: polyvinyl alcohol and Viton (fluorocarbon rubber). A material that may withstand permeation for more than 4 but fewer than 8 hours is Teflon (polytetrafluoroethylene). Butyl rubber, natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by 1,3-dichloropropene.

If 1,3-dichloropropene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 1,3-dichloropropene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 1,3-dichloropropene. Contact lenses should not be worn when working with this material.

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