

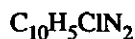
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROBENZYLIDENE MALONONITRILE

INTRODUCTION

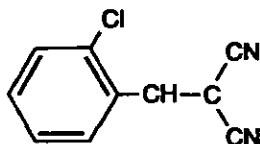
This guideline summarizes pertinent information about o-chlorobenzylidene malononitrile for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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



• Structure



• Synonyms

CS; OCBM; (o-chlorobenzal)malononitrile; beta,beta-dicyano-o-chlorostyrene

• Identifiers

1. CAS No.: 2698-41-1

2. RTECS No.: OO3675000

3. DOT UN: None

4. DOT label: None

• Appearance and odor

o-Chlorobenzylidene malononitrile is a white, crystalline solid with a pepper-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 188.6

2. Boiling point (760 mm Hg): 310° to 315°C (590° to 599°F)

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

4. Vapor density (air = 1 at boiling point of o-chlorobenzylidene malononitrile): 6.5

5. Melting point: 95° to 96°C (203° to 205°F)

6. Vapor pressure at 20°C (68°F): 0.000034 mm Hg

7. Solubility: Insoluble in water; soluble in acetone, benzene, ethyl acetate, dioxane, and methylene chloride.

8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

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

Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of o-chlorobenzylidene malononitrile with strong oxidizers causes a violent reaction.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine, cyanide, and nitrogen oxides) may be released in a fire involving o-chlorobenzylidene malononitrile.
4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to o-chlorobenzylidene malononitrile.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: No information is available on the appropriate extinguishant to use for a fire involving o-chlorobenzylidene malononitrile.

Fires involving o-chlorobenzylidene malononitrile should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorobenzylidene malononitrile.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for o-chlorobenzylidene malononitrile is 0.05 ppm parts of air (0.4 mg/m³) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended expo-

sure limit (REL) of 0.05 ppm (0.4 mg/m³) as a ceiling limit. 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 [NIOSH 1992].

• ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned a ceiling limit value of 0.05 ppm (0.39 mg/m³), which should not be exceeded during any part of the working exposure. The ACGIH has also assigned a "Skin" notation [ACGIH 1993].

• Rationale for limits

The OSHA, NIOSH, and ACGIH limits are based on the risk of eye and respiratory tract irritation associated with exposure to o-chlorobenzylidene malononitrile [54 Fed. Reg. 2457; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to o-chlorobenzylidene malononitrile can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals:* o-Chlorobenzylidene malononitrile is a severe lacrimator and upper respiratory tract irritant. Human eyes are more sensitive to o-chlorobenzylidene malononitrile-induced irritation than rabbit, rat, or guinea pig eyes; however, even in extreme exposures, eye injuries are superficial and reversible [Grant 1986]. The lowest lethal concentration in rats is 1,806 mg/m³ for 45 min [NIOSH 1993]. Rats exposed to a 1800-mg/m³ concentration of this substance for 10 min survived, but a 60-min exposure to 2,700 mg/m³ killed all of the animals [Hathaway et al. 1991]. The most recent oral LD₅₀s reported for rats are 1,366 mg/kg (male) and 1,284 mg/kg (female) [ACGIH 1991]. Earlier studies in rats reported oral LD₅₀s ranging from 178 to 717 mg/kg [NIOSH 1993]. This substance causes systemic cyanide poisoning when animals are exposed to high doses; the mechanism of action appears to be the release of hydrocyanic acid from one or both nitriles of the malononitrile [Gosselin et al. 1984]. Mice that were injected intraperitoneally or intravenously with o-chlorobenzylidene malononitrile or were exposed

to a concentration of 20,000 mg/m³/min of the aerosol had cyanide in their blood and urine [ACGIH 1991].

2. *Effects on Humans:* o-Chlorobenzylidene malononitrile (OCBM) is a potent lacrimator and sternutator, and a peripheral sensory irritant in humans. This substance is the active ingredient in tear gas; exposure causes an immediate, disabling irritation of the eyes and respiratory tract in humans, but no OCBM-related deaths have been reported [Grant 1986]. Exposure to an OCBM concentration of 1.5 mg/m³ for 90 min resulted in headaches in three of four men exposed and caused nose and eye irritation in one man [ACGIH 1991; Hathaway et al. 1991]. Contact of OCBM with the skin resulted in a burning sensation that was greatly aggravated by moisture, erythema, and vesiculation resembling second degree burns were produced [Hathaway et al. 1991]. Workers handling OCBM have developed skin sensitization; the resulting dermatitis involves the arms and neck [ACGIH 1991]. Concentrations of 4.3 to 6.7 mg/m³ could barely be tolerated when this concentration was reached gradually over a 30-min period; subjects reported conjunctivitis, involuntary closing of the eyes, burning in the throat, cough, and chest constriction [Hathaway et al. 1991]. Concentrations greater than 10 mg/m³ are extremely irritating and have been found to be intolerable for more than 30 seconds under test conditions; the eye irritation disappeared within an hour after cessation of exposure, and respiratory effects disappeared within a few minutes [Grant 1986].

• **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to o-chlorobenzylidene malononitrile may cause pain and burning of the eyes, excessive tearing, conjunctivitis, involuntary closing of the eyes, excessive salivation, nausea, vomiting, nose and throat irritation, cough, chest constriction, dizziness, headache, and redness and burning of the skin with blister formation.
2. *Chronic exposure:* Chronic exposure to o-chlorobenzylidene malononitrile may cause dermatitis of the face and arms.

• **Emergency procedures:**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation

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

1. *Eye exposure:* Irritation may result. **Immediately and thoroughly** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.
2. *Skin exposure:* Irritation may result. **Immediately and thoroughly** wash contaminated skin with soap and water
3. *Inhalation exposure:* Move victim to fresh air **immediately**. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

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

4. *Ingestion exposure:* Take the following steps if o-chlorobenzylidene malononitrile or any material containing it is ingested:

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

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

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

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

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 o-chlorobenzylidene

dene malononitrile and may result in worker exposures to this substance:

—Manufacturing and formulation of *o*-chlorobenzylidene malononitrile for use as a riot control agent

The following methods are effective in controlling worker exposures to *o*-chlorobenzylidene malononitrile, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. *Industrial ventilation—a manual of recommended practice*. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. *Industrial ventilation—a self study companion*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. *Design of industrial ventilation systems*. New York, NY: Industrial Press, Inc.
4. 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*. Chicago, IL: National Safety Council.

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 *o*-chlorobenzylidene malononitrile, 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 *o*-chlorobenzylidene malononitrile at or below the prescribed exposure limit. The 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 *o*-chlorobenzylidene malononitrile exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of *o*-chlorobenzylidene malononitrile on the eyes, skin, or respiratory tract. Current health status should be compared with the base-

line 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. *o*-Chlorobenzylidene malononitrile can be detected in the blood of exposed individuals; however, blood concentrations of this substance do not correlate well with airborne concentrations. Therefore, no biological monitoring test acceptable for routine use has yet been developed for *o*-chlorobenzylidene malononitrile.

- **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. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne *o*-chlorobenzylidene malononitrile is determined by using a polytetrafluoroethylene (FA) 1-micron filter in series with a Tenax GC tube (70/35-mg sections, 35/60 mesh). Samples are collected at a maximum flow rate of 1.5 liter/min until a maximum air volume of 90 liters is collected. The samples are desorbed with 20% methylene chloride in hexane. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is approximately 0.3 µg/sample. This method is described in NIOSH Method P&CAM 304 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If *o*-chlorobenzylidene malononitrile contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with *o*-chlorobenzylidene malononitrile should be removed immediately; provisions should be made for safely removing this chemical from these articles.

A worker who handles *o*-chlorobenzylidene malononitrile 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 *o*-chlorobenzylidene malononitrile is handled, processed, or stored.

STORAGE

o-Chlorobenzylidene malononitrile should be stored in a cool, dry, well-ventilated area or in a refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of *o*-chlorobenzylidene malononitrile should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained *o*-chlorobenzylidene malononitrile may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

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

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.
5. For large spills, build dikes far ahead of the spill to contain the *o*-chlorobenzylidene malononitrile 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**

o-Chlorobenzylidene malononitrile 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**

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

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

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorobenzylidene malononitrile 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. Although o-chlorobenzylidene malononitrile is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

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 addi-

tion, 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 o-chlorobenzylidene malononitrile 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 emergency situations. 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 1901.134]. 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 clothing should be worn to prevent any skin contact with o-chlorobenzylidene malononitrile. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommenda-

tions, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorobenzylidene malononitrile permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorobenzylidene malononitrile.

If o-chlorobenzylidene malononitrile 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 o-chlorobenzylidene malononitrile might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorobenzylidene malononitrile. Contact lenses should not be worn if the potential exists for o-chlorobenzylidene malononitrile exposure.

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