

Occupational Health Guideline for o-Chlorobenzylidene Malononitrile

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: $C_{10}H_5ClN_2$
- Synonyms: OCBM; CS
- Appearance and odor: White solid with a pepper odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-chlorobenzylidene malononitrile is 0.05 part of o-chlorobenzylidene malononitrile per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of o-chlorobenzylidene malononitrile per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for o-chlorobenzylidene malononitrile from 0.05 ppm as a time-weighted average value to 0.05 ppm as a ceiling

HEALTH HAZARD INFORMATION

• Routes of exposure

o-Chlorobenzylidene malononitrile 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: o-Chlorobenzylidene malononitrile causes headache, eye irritation (with eye watering and burning), burning of the throat, sneezing, coughing, and a constricting sensation in the chest. There may be delayed breathing difficulties. Burning of the skin also

occurs and is greatly increased by the presence of moisture. Heavy exposures may cause skin blistering.

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 o-chlorobenzylidene malononitrile.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to o-chlorobenzylidene malononitrile 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 o-chlorobenzylidene malononitrile exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of o-chlorobenzylidene malononitrile might cause exacerbation of symptoms due to its irritant properties.

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

—Eye disease: o-Chlorobenzylidene malononitrile is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

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

• Summary of toxicology

o-Chlorobenzylidene malononitrile aerosol is a potent lacrimator and respiratory irritant. In human experiments, concentrations ranging from 4.3 to 6.7 mg/m^3 were barely tolerated when reached gradually over a period of 30 minutes; a burning sensation and deep pain in the eyes persisted for 2 to 5 minutes following

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.

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cessation of exposure, severe conjunctival injection for 25 to 30 minutes, and erythema of the eyelids with some blepharospasm for 1 hour; there was a burning sensation in the throat with cough, followed by a constricting sensation in the chest; no therapy other than removal from exposure was necessary. At a concentration of 1.5 mg/m³, 3 of 4 men developed headache during a 90-minute exposure; one subject developed slight eye and nose irritation. On the skin, the powder caused a burning sensation which was greatly aggravated by moisture; erythema and vesiculation resembling second-degree burns were produced.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 188.5
2. Boiling point (760 mm Hg): 310– 315 C (590– 599 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of o-chlorobenzylidene malononitrile): 6.5
5. Melting point: 93– 95 C (199– 203 F)
6. Vapor pressure at 20 C (68 F): Much less than 1
7. Solubility in water, g/100 g water at 20 C (68 F):

Insoluble

8. Evaporation rate (butyl acetate = 1): Data not available

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, oxides of nitrogen, and carbon monoxide) may be released in a fire involving o-chlorobenzylidene malononitrile.
4. Special precautions: None

• Flammability

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Minimum explosive concentration: 0.025 g/l
4. Extinguishant: Carbon dioxide, dry chemical

• Warning properties

1. Odor Threshold: No information is available concerning the odor threshold of OCBM.
2. Eye Irritation Level: According to the *Documentation of TLV's*, in an experiment with human volunteers, "one subject developed slight eye and nose irritation" during a 90-minute exposure to 1.5 mg/m³. Since the compound has such highly irritant properties, "concentrations ranging between 4.3 to 6.7 mg/m³ could not be tolerated unless the concentration was reached gradually over a period of 30 minutes."
3. Other Information: Deichmann and Gerarde state that inhalation of o-chlorobenzylidene malononitrile causes "'burning' in the throat and progressing down the respiratory tract," but no quantitative information is given concerning the threshold of these irritant effects. Grant reports that humans exposed to concentrations

greater than 10 mg/m³ experienced extreme burning and pain in the chest, as well as in the eyes.

4. Evaluation of Warning Properties: Since information concerning the odor threshold of OCBM is not available, and since only slight eye irritation has been observed in only one human subject at a concentration several times greater than the permissible exposure, OCBM could be treated as a material with poor 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 o-chlorobenzylidene malononitrile is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

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 o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile.

- If employees' clothing has had any possibility of being contaminated with o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing which has had any possibility of being contaminated with o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of o-chlorobenzylidene malononitrile from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-chlorobenzylidene malononitrile, the person performing the operation should be informed of o-chlorobenzylidene malononitrile's hazardous properties.

- Non-impervious clothing which becomes contaminated with o-chlorobenzylidene malononitrile should be removed promptly and not reworn until the o-chlorobenzylidene malononitrile is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile may contact the eyes.

SANITATION

- Workers subject to skin contact with o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile should wash with soap or mild detergent and water any areas of the body which may have contacted o-chlorobenzylidene malononitrile at the end of each work day.

- Skin that becomes contaminated with o-chlorobenzylidene malononitrile should be promptly washed or showered with soap or mild detergent and water to remove any o-chlorobenzylidene malononitrile.

- Eating and smoking should not be permitted in areas where o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile are handled, processed, or stored.

- Employees who handle o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation

Use as a harassing agent in civil disturbances and wars

Controls

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 o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If o-chlorobenzylidene malononitrile or liquids containing o-chlorobenzylidene malononitrile penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of o-chlorobenzylidene malononitrile, 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 o-chlorobenzylidene malononitrile has been swallowed, 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 AND DISPOSAL PROCEDURES

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

- If o-chlorobenzylidene malononitrile is spilled, the following steps should be taken:

1. Ventilate area of spill.

2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

3. Decontaminate area of spill: (a) by washing with a 5% solution of sodium hydroxide in 50/50 ethyl alcohol/water; or (b) by adding flake sodium hydroxide to a solution or slurry of the spill in isopropyl alcohol; or (c) by covering the spill with a 10% solution of sodium hydroxide in 50/50 isopropyl alcohol/water and letting stand 20 minutes before flushing with water.

• Waste disposal and neutralization methods:

o-Chlorobenzylidene malononitrile may be disposed of:

1. By making packages of *o*-chlorobenzylidene malononitrile in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving *o*-chlorobenzylidene malononitrile in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

3. By mixing solid with 5 parts of a 10% solution of monoethanolamine in water containing 0.3% of non-ionic detergent.

4. By stirring one pound of solid for 2 hours in one gallon of a 5–15% solution of sodium hydroxide in ethylene glycol, ethyl alcohol, or methyl alcohol.

REFERENCES

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- U.S. Army, Edgewood Arsenal: "Safety Guide for Processing, Filling, Handling and Decontamination of CS and CS1," CML C SD 385-12, February 1961.

RESPIRATORY PROTECTION FOR o-CHLOROBENZYLIDENE MALONONITRILE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Particulate or Vapor Concentration	
2 mg/m ³ (0.24 ppm) or less	<p>A chemical cartridge respirator with a full facepiece and a combination organic vapor cartridge(s) with high efficiency particulate filters.</p> <p>A gas mask with a chin-style or a front- or back-mounted organic vapor canister and high efficiency particulate filter.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
Greater than 2 mg/m ³ (0.24 ppm) or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>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.</p>
Fire Fighting	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p>
Escape	<p>Any gas mask with a full facepiece providing protection against organic vapors and particulates.</p> <p>Any escape self-contained breathing apparatus with a full facepiece.</p>

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

