

# Occupational Health Guideline for Methylene Bisphenyl Isocyanate (MDI)

## 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:  $\text{NCOC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NCO}$
- Synonyms: MDI; 4,4-diphenylmethane diisocyanate; methylene bis (4-phenyl isocyanate); 4,4-diisocyanatodiphenylmethane
- Appearance and odor: White to light-yellow flakes with no odor.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene bisphenyl isocyanate is a ceiling level of 0.02 part of methylene bisphenyl isocyanate per million parts of air (ppm). This may also be expressed as 0.2 milligram of methylene bisphenyl isocyanate per cubic meter of air ( $\text{mg}/\text{m}^3$ ).

## HEALTH HAZARD INFORMATION

- **Routes of exposure**  
Methylene bisphenyl isocyanate 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:** Exposure to methylene bisphenyl isocyanate may make a person allergic to it and produce wheezing, shortness of breath, and coughing. It may also cause irritation of the eyes and lungs, upset stomach, vomiting, possibly fever, stuffiness of the nose, sore throat, a feeling of tightness in the chest, cough, shortness of breath and wheezing. Such symptoms may be delayed up to eight hours after the person has been exposed.

2. **Long-term Exposure:** A person may become increasingly sensitive or allergic to methylene bisphenyl isocyanate. Chronic exposure to it may lead to permanent breathing or chest problems. Repeated or prolonged exposure of the skin to methylene bisphenyl isocyanate may cause a skin rash.

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 methylene bisphenyl isocyanate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylene bisphenyl isocyanate 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. Persons with a history of asthma, allergies, or known sensitization to methylene bisphenyl isocyanate would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Methylene bisphenyl isocyanate may cause lung damage in humans. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methylene bisphenyl isocyanate is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Methylene bisphenyl isocyanate (MDI) vapor is a potent respiratory sensitizer. It also is a strong irritant of the eyes, mucous membranes, and skin and can cause

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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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pulmonary edema. Exposure of humans to high concentrations causes cough, dyspnea, increased secretions, and chest pain. Isocyanates cause pulmonary sensitization in susceptible individuals; should this occur, further exposure should be avoided, since extremely low levels of exposure may trigger an asthmatic episode; cross sensitization to unrelated materials probably does not occur. The liquid in contact with the eye may cause an irritation.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 250.25
2. Boiling point (760 mm Hg): 172 C (341.6 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of methylene bisphenyl isocyanate): 8.6
5. Melting point: 37 C (98.6 F)
6. Vapor pressure at 20 C (68 F): 0.05 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity

1. Conditions contributing to instability: Temperatures above 37.8 C (100 F)
2. Incompatibilities: Avoid contact with strong alkalis, acids, and alcohol.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving methylene bisphenyl isocyanate.
4. Special precautions: Liquid methylene bisphenyl isocyanate will attack some forms of plastics, rubber, and coatings.

### • Flammability

1. Flash point: 202 C (395.6 F) (open cup)
2. Autoignition temperature: 240 C (464 F)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Carbon dioxide, dry chemical, or inert gas. For large fires, water in the form of spray should be used.

### • Warning properties

- 1; Odor Threshold: No quantitative information is available.
- 2; Irritation Levels: By analogy to TDI, which, according to Grant, causes irritation of the eyes and nose beginning at 0.05 ppm to 0.1 ppm, MDI is assumed to produce eye and nose irritation at the same levels.
- 3; Evaluation of Warning Properties: MDI is treated as a material with poor warning properties, for the purposes of this guideline. By analogy with TDI, MDI is assumed to produce eye and nose irritation within several times the permissible exposure limit, but the permissible exposure is a ceiling concentration.

## MONITORING AND MEASUREMENT PROCEDURES

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene bisphenyl isocyanate. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

### • Method

At the time of publication of this guideline, no measurement method for methylene bisphenyl isocyanate had been published by NIOSH.

## 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 solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate, where skin contact may occur.
- If employees' clothing may have become contaminated with methylene bisphenyl isocyanate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with methylene bisphenyl isocyanate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylene bisphenyl isocyanate from

the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylene bisphenyl isocyanate, the person performing the operation should be informed of methylene bisphenyl isocyanate's hazardous properties.

- Non-impervious clothing which becomes contaminated with methylene bisphenyl isocyanate should be removed promptly and not reworn until the methylene bisphenyl isocyanate is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate contacting the eyes.

## SANITATION

- Skin that becomes wet with methylene bisphenyl isocyanate should be promptly washed or showered with soap or mild detergent and water to remove any methylene bisphenyl isocyanate.
- Employees who handle solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate 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 methylene bisphenyl isocyanate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during in place spraying of urethane foams	Local exhaust ventilation; respiratory protective equipment
Liberation during in place molding of urethane foams	Local exhaust ventilation; dilution ventilation
Liberation during application of polyisocyanate lacquer sealant finishes	Local exhaust ventilation; respiratory protective equipment
Liberation during shake-out and core knock-out operations at foundries using MDI-oil-base-no-bake binding systems	Local exhaust ventilation; respiratory protective equipment
Liberation during manufacture of lacquer	Process enclosure; local exhaust ventilation
Liberation during production of component chemicals for foam systems	Local exhaust ventilation; process enclosure

## Operation

Liberation during casting of high-density polyurethane elastomers

Liberation following combustion of urethane foams in fires or thermal decomposition to salvage metal inserts

Liberation of unreacted vapor during cutting and fabricating of polyurethane foams

Liberation during curing process; during flame lamination of fabrics

## Controls

Process enclosure; local exhaust ventilation

Air-supply respiratory protective equipment or local exhaust ventilation

Local exhaust ventilation; respiratory protective equipment

Process enclosure; local ventilation

## 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 methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate get 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 methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

### • Breathing

If a person breathes in large amounts of methylene bisphenyl isocyanate, 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 methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate have 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 some-

one 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 methylene bisphenyl isocyanate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

2. 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.

- Waste disposal methods:

Methylene bisphenyl isocyanate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

## REFERENCES

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## RESPIRATORY PROTECTION FOR METHYLENE BISPHENYL ISOCYANATE (MDI)

Condition	Minimum Respiratory Protection* Required Above 0.02 ppm
Vapor or Particulate Concentration	
1 ppm (10 mg/m <sup>3</sup> ) or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm (100 mg/m <sup>3</sup> ) 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 10 ppm (100 mg/m <sup>3</sup> ) 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 and particulates. Any escape self-contained breathing apparatus.

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

