Occupational Health Guideline for Methyl Isocyanate

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: CH₂NCO
- Synonyms: None
- Appearance and odor: Colorless liquid with a sharp odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl isocyanate is 0.02 part of methyl isocyanate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.05 milligram of methyl isocyanate per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- Routes of exposure
  Methyl 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
  Inhalation of methyl isocyanate vapors may cause irritation of the eyes, nose, throat, and lungs. Cough, shortness of breath, increased phlegm and chest pain may be present. The liquid splashed in the eyes may cause permanent damage. The liquid splashed on the skin may cause irritation. Exposure to methyl isocyanate may cause a person to become allergic to it so that extremely low levels of exposure may cause an asthmatic attack.
  - 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 methyl isocyanate.
  - Recommended medical surveillance
    The following medical procedures should be made available to each employee who is exposed to methyl 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 methyl isocyanate would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.
      - 14" x 17" chest roentgenogram: Methyl isocyanate causes lung damage in animals. Surveillance of the lungs is indicated.
    2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.
  - Summary of toxicology
    Methyl isocyanate vapor is an intense lacrimator and irritates the eyes, mucous membranes, and skin. It can cause pulmonary irritation and sensitization. In rats exposed for 4 hours, the LC50 was 5 ppm; effects were injury to the lungs and subsequent pulmonary edema. Exposure of humans to high concentrations can cause 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 expo-

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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National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
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sure may trigger an asthmatic episode; cross sensitization to unrelated materials probably does not occur. Experimental exposure of four human subjects for 1 to 5 minutes caused the following effects: 0.4 ppm, no effects; 2 ppm, lacrimation, irritation of the nose and throat; 4 ppm, symptoms of irritation more marked; 21 ppm, unbearable irritation of eyes, nose, and throat. A cotton plug saturated with the liquid was applied to the ear of a rabbit for 30 minutes and caused erythema, edema, necrosis, and perforation; a few drops of the liquid on the ear of a rabbit caused destruction of tissue. The liquid in contact with the eye may cause permanent damage.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data
  1. Molecular weight: 57.1
  2. Boiling point (760 mm Hg): 39 C (102 F)
  3. Specific gravity (water = 1): 0.96
  4. Vapor density (air = 1 at boiling point of methyl isocyanate): 2.0
  5. Melting point: -80 C (-112 F)
  6. Vapor pressure at 20 C (68 F): 348 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F):
     6.7 (reacts slowly)
  8. Evaporation rate (butyl acetate = 1): 26.8
• Reactivity
  1. Conditions contributing to instability: Elevated
temperatures may cause methyl isocyanate to polymerize and burst container.
  2. Incompatibilities: Contact with water causes formation of carbon dioxide and methylamine gases. The reaction is much more rapid in the presence of acids, alkalies, and amines. Contact with iron, tin, copper (or salts of these elements) and with certain other catalysts (such as triphenylarsenic oxide, triethylphosphine, and tributyltin oxide) may cause violent polymerization.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving methyl isocyanate.
  4. Special precautions: Methyl isocyanate will attack some forms of plastics, rubber, and coatings.
• Flammability
  1. Flash point: Less than -18 C (0 F) (open cup)
  2. Autoignition temperature: 555 C (995 F)
  3. Flammable limits in air, % by volume: Lower: 5.3;
     Upper: 26
  4. Extinguisher: Carbon dioxide, dry chemical, foam
• Warning properties
  1. Odor Threshold: The Documentation of TLV's states that humans exposed to 0.4 ppm methyl isocyanate for periods up to 5 minutes could not detect the odor. Even at a concentration of 2 ppm, the odor was not perceived.
  2. Irritation Levels: At a concentration of 0.4 ppm,
eye, nose, and throat irritation was not experienced by human subjects who were exposed for periods up to 5 minutes. The Documentation of TLV's states that "at 2 ppm no odor was detected, but the subjects experienced irritation and lacrimation. At 4 ppm the symptoms of irritation were more marked. Exposure was unbearable at 21 ppm."

3. Evaluation of Warning Properties: Since the odor and irritation thresholds of methyl isocyanate are not within 3 times the permissible exposure limit, for the purposes of this guideline, methyl isocyanate is 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
At the time of publication of this guideline, no measurement method for methyl 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 any possibility of skin contact with liquid methyl isocyanate.
• Clothing wet with liquid methyl isocyanate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl isocyanate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl isocyanate, the person performing the operation should be informed of methyl isocyanate’s hazardous properties.

• If employees’ clothing has had any possibility of being contaminated with liquid methyl isocyanate, employees should change into uncontaminated clothing before leaving the work premises.

• Any clothing which becomes wet with and non-impervious clothing which becomes contaminated with liquid methyl isocyanate should be removed immediately and not re-worn until the methyl isocyanate 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 methyl isocyanate contacting the eyes.

• Where there is any possibility that employees’ eyes may be exposed to liquid methyl isocyanate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid methyl isocyanate should be immediately washed or showered to remove any methyl isocyanate.

• Employees who handle liquid methyl isocyanate should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
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<tbody>
<tr>
<td>Use as a cross-linking agent; additive to adhesives in polymer technology; use in organic synthesis</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and seek for first aid or medical assistance.

• Eye Exposure

If liquid methyl isocyanate gets 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 methyl isocyanate gets on the skin, immediately flush the contaminated skin with large amounts of water. If liquid methyl isocyanate soaks through the clothing, remove the clothing immediately and flush the skin with large amounts of water. If irritation persists after washing, get medical attention immediately.

• Breathing

If a person breathes in large amounts of methyl 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 liquid methyl isocyanate 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 methyl isocyanate is 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 equipped with an appropriate effluent gas cleaning device. Methyl isocyanate 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 methyl isocyanate vapors are permitted.

• Waste disposal method:

Methyl isocyanate may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
REFERENCES


RESPIRATORY PROTECTION FOR METHYL ISOCYANATE

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 0.02 ppm</th>
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<tbody>
<tr>
<td>Vapor Concentration</td>
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<tr>
<td>0.2 ppm or less</td>
<td>Any supplied-air respirator. Any self-contained breathing apparatus.</td>
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<tr>
<td>1 ppm or less</td>
<td>Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.</td>
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<tr>
<td>20 ppm or less</td>
<td>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.</td>
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<tr>
<td>Greater than 20 ppm or entry and escape from unknown concentrations</td>
<td>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.</td>
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<tr>
<td>Fire Fighting</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td>Escape</td>
<td>Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.</td>
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*Only NIOSH-approved or MSHA-approved equipment should be used.