Guidance for Working with MDI: Things You Should Know

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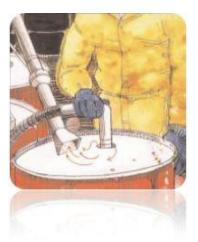
Purpose

The Center for the Polyurethanes Industry (CPI) prepared this guidance to provide information about important health and safety considerations when working with MDI. It supplements the comprehensive information contained in your supplier's Safety Data Sheets (SDSs), which are the primary source of information for specific MDI distribution and handling issues. Throughout this document, the term MDI is used to address

both monomeric MDI and polymeric MDI.







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Identifying MDI

Methylene diphenyl diisocyanate is commonly referred to as MDI. Monomeric MDI is a white to yellowish solid at room temperature with no odor. Polymeric MDI is a mixture of monomeric MDI as well as larger molecular weight oligomers of MDI, and is a brownish liquid at room temperature and may have a slight odor. Commercial MDI products are often mixtures of monomeric and polymeric MDI and can contain other additives as well. The odor threshold (the ability to smell MDI) is significantly greater than the permissible exposure limit and threshold limit value. The table below illustrates some key chemical and physical properties of monomeric and polymeric MDI:

	Monomeric 4,4'- MDI	Polymeric MDI
Physical State	Solid at ambient conditions	Liquid
Molecular Weight	250	varies
Boiling Point	> 300 °C	> 300 °C
Freezing/Melting Point	40 °C	5°C
Specific Gravity	1.33 @ 68°F (20°C)	1.24 @ 68°F (20°C)
Density	9.8 lbs/gal (50°C)	
Vapor Pressure	4.65x10-6 mm Hg at 68°F (20°C)	2.33x10-6 mm Hg at 68°F (20°C)
Viscosity	4.7 to 5.0 mPas @ 122°F (50°C)	100 to 250 mPas @ 77°F (25°C)
Solubility in Water	Reacts with water; not soluble. Reaction with water produces CO2 and polyurea.	Reacts with water; not soluble. Reaction with water produces CO2 and polyurea.
Flash Point	412°F (211°C)	406°F (208°C)
CAS #	101-68-8	9016-87-9

Source: MDI and TDI: Safety, Health and the Environment. A Source Book and Practical Guide. Dennis C. Allport, David S. Gilbert, Susan M. Outterside, 2003.

Recognizing Potential Health Hazards

Overexposure to MDI vapor, liquid or aerosol can be harmful to your health. There are four possible routes of exposure:

- Inhalation
- Eye contact
- Skin contact
- Ingestion

Below are the potential effects of overexposure and some first-aid considerations:

Inhalation:

As illustrated in the previous table, the vapor pressure of MDI is very low. Therefore, it is not likely to produce MDI vapors in the breathing zone above the occupational exposure limit when handled at room temperature. Operations/tasks that are likely to result in high airborne concentrations of MDI include applications that involve spraying, heating (i.e., closed molding applications) or when handled in work areas with poor ventilation.

The odor threshold of MDI is above the established exposure limits. Therefore, odor should never be used to indicate the presence of MDI. Exposure limits are set by regulatory organizations like the Occupational Safety and Health Administration (OSHA) and other professional (non-regulatory) organizations such as the American Conference of Governmental Industrial Hygienists (ACGIH). Exposure limits typically define the maximum airborne concentrations of chemical substances and represent conditions to which it is believed that nearly all workers, without use of respiratory protection, may be repeatedly exposed without adverse health effects.

Airborne exposure to MDI may include possible respiratory irritation effects such as:

- nose irritation
- coughing
- chest tightness or discomfort
- shortness of breath

Overexposure to MDI may cause you to become sensitized or "allergic." If sensitized, you may feel tightness in your chest and have difficulty breathing when exposed to MDI even at low levels. Effects may be either immediate and/or delayed for several hours. If diagnosed with sensitization, avoid exposure to all diisocyanates.

If you suspect someone has become overexposed, move the person to an area free from further exposure. Seek medical attention immediately. A qualified person may administer oxygen or artificial respiration as needed.

Eye Contact:

Getting liquid MDI in your eyes may be painful and could cause temporary corneal injury. If you get MDI in your eyes, flush them immediately with a continuous flow of low pressure water, preferably from an eyewash station, for at least 15 minutes. Seek medical attention immediately.

Skin Contact:

Getting MDI on your skin may play a role in the development of skin sensitization, an allergic reaction. In addition, animal tests have indicated that skin contact with MDI may play a role in the development of respiratory sensitization. Getting MDI on your skin may also cause discoloration, redness, swelling, or itching. If direct skin contact with isocyanates occurs, immediately remove contaminated clothing and shoes. Wipe off the isocyanate product from the skin using dry towels or other similar absorbent fabric. If readily available, apply a polyglycol-based cleanser or corn oil. Wash with soap and warm water and pat dry. If a polyglycol-based cleanser is not available, wash with soap and warm water for 15 minutes. If available, use a wipe test pad to verify decontamination is complete. Seek medical attention if irritation develops. Discard or wash contaminated clothing before reuse. For larger exposures, use an emergency shower.

Ingestion:

Although unlikely, accidental ingestion of MDI can occur. Swallowing MDI can cause irritation in your mouth, throat, and stomach. If ingestion occurs, rinse the mouth with water; do not try to induce vomiting. Do not give anything by mouth to an unconscious person. Seek medical attention immediately.



Protecting Yourself from MDI Overexposure

Overexposure to airborne MDI can occur in inadequately ventilated environments when MDI is sprayed, aerosolized, or heated. In addition, overexposure can occur when there is direct skin contact with liquid MDI. Reducing or eliminating your exposure risk will help prevent the potential of adverse health effects.

Where there is a potential risk of exposure to airborne MDI above applicable exposure limits, consider using (at a minimum):

- An approved respirator, either air-supplied or air-purifying. The type of respiratory protection will depend upon the maximum exposure concentration.
 Consult your company safety professional or the product SDS for guidance.
- Elevated airborne concentrations may cause irritation of the eyes; therefore, eye protection may also be needed, if not already provided by the respirator.
- For more details on the use of air purifying respirators under the OSHA Standard, please refer to the CPI document Guidance for Developing a Written Respiratory Program (AX 501).

Where there is a risk of skin and eye contact with liquid MDI, consider using (at a minimum):

- MDI resistant chemical gloves (see CPI document Guidance for Selection of Personal Protective Equipment for MDI Users, AX-178).
- In situations where there is splash potential (e.g., when directly handling liquid product), workers should wear chemical splash goggles and, depending upon the extent of potential contact, a faceshield. These situations may include line-breaking (transfer hose disconnect), transfer of material using a drum pump, etc.
- If there is potential for more extensive exposure, consider using the following:
 - o MDI-resistant long-sleeve coveralls or full body suit (see CPI document AX-178).
 - o MDI-resistant fitted boots.
 - Head covering.

In spray applications, respiratory protection, eye protection, and complete skin protection are necessary. Visit spraypolyurethane.org for additional health and safety information on spray polyurethane foam.

Understanding Potential Reactivity Hazards

MDI is a reactive chemical and it is important that it is stored and handled properly. Dangerous buildup of heat and/or pressure (see "Caution" noted below) within storage containers or closed process vessels can result from improper mixing or contact with:

- Acids, inorganic bases (such as sodium hydroxide or potassium hydroxide), and ammonia
- Polyetheramines, amine catalysts and other amines
- Magnesium, aluminum, and their alloys
- Other metal salts, especially halides (such as tin, iron, aluminum and zinc chlorides)
- All strong oxidizing agents (such as bleach or chlorine)
- Polyols and other alcohols
- Water (typically a slower reaction that releases carbon dioxide gas)

Caution: Resealing MDI containers contaminated with any of the above materials can cause a buildup of pressure in the container and cause it to forcibly rupture. All forms of MDI can also self-react in a fire or at very high temperatures which releases carbon dioxide and causes the buildup of pressure in sealed containers sufficient to cause a forcible rupture.

Handling, Unloading and Storing MDI

To minimize hazards when handling, unloading, storing, or disposing of MDI consider the following:

- Wearing protective clothing
- Following employers' established procedures for normal operations, maintenance, loading/ unloading, sampling, special operations, and emergencies
- Using appropriate checklists as the steps are being completed
- Inspecting equipment to ensure operating integrity following maintenance procedures
- Maintaining good housekeeping
- Participating in relevant training programs
- Following all safety precautions for handling MDI until empty drums are resealed or ready for reclamation
- Handling and storing drums in a wellventilated and dry area with spill containment
- Following manufacturer's instructions for MDI storage temperature
- Checking drum shipments for leakage
- Using plugs/caps on terminal valves or fittings and bleed valves
- Keeping drum overpacks available
- Keeping drums segregated from containers of material that are incompatible with MDI
- Providing secondary containment
- Always review the manufacturer's SDS

When handling MDI, DO NOT:

- use pressure to empty drums
- store MDI in open-head drums
- cut empty MDI drums with a torch
- use empty MDI drums from a worksite for personal use such as a barbecue pit, flower box, trash barrel, etc.

Empty drums should be handled by a qualified drum reconditioner. Contact the Reusable Industrial Packaging Association (RIPA – www.reusablepackaging.org) to locate a drum reconditioner near you.



Responding to Emergencies

Fires, spills, bulging drums, and other emergencies involving MDI require immediate responses. If you are not a trained, designated emergency responder, leave the area immediately and notify the appropriate emergency response personnel.

If you need assistance with a spill or other emergency involving MDI, call CHEMTREC at 1-800-424-9300.

CHEMTREC operators are available 24 hours a day, seven days a week.





Legal Notice

This guidance document was prepared by the American Chemistry Council's Center for the Polyurethanes Industry. It is intended to provide general information to professional persons who may handle MDI. It is not intended to serve as a substitute for in-depth training or specific handling or storage requirements, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a "how-to" manual, nor is it a prescriptive guide. All persons involved in handling MDI have an independent obligation to ascertain that their actions are in compliance with current federal, state and local laws and regulations and should consult with legal counsel concerning such matters. The guidance is necessarily general in nature and individual companies may vary their approach with respect to particular practices based on specific factual circumstance, the practicality and effectiveness of particular actions and economic and technological feasibility.

