Product Safety Assessment

MDI-Based Isocyanate Products

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Names
- CAS No. 26447-40-5 (for ISONATE™ MDI monomeric MDI products)
- ISONATE™ MDI isocyanate products
- Methylene diphenyl diisocyanate
- Diphenylmethane diisocyanate
- 1,1'-methylene bis (isocyanatobenzene)

- CAS No. 9016-87-9 (for PAPI™ polymeric MDI products)
- PAPI™ polymeric MDI products
- Methylene bis(p-phenyl isocyanate)
- Methylene bisphenyl isocyanate

Product Overview
- This product safety assessment covers a group of products that share similar characteristics and properties. For information about a specific product, please refer to the product Safety Data Sheet (SDS). Pure MDI is a solid at room temperature with a melting point of 38°C. Liquid MDI products (including melted pure and modified MDI) are colorless to yellow liquids with a mild odor. Polymeric MDI is a brown liquid. In the United States, MDI is the standard abbreviation for "pure" diphenylmethane diisocyanate. See Product Description.
- MDI products are building blocks in a wide variety of thermoplastic polymers suitable for extrusion, injection molding, and solution applications. The rigid foams market consumes more than 50 percent of manufactured MDI. See Product Uses.
- Diphenylmethane diisocyanate, the principal active ingredient in MDI products, is a highly reactive and a potentially hazardous material that has the potential to adversely affect or injure the eyes, skin, and respiratory tract if appropriate safe handling and use instructions are not followed, or if appropriate safe handling and use precautions are not employed. See Health Information.
- If released to the environment, MDI reacts with water to form insoluble polyureas that are chemically and biologically inert. These polyureas do not accumulate in the food chain, and are practically non-toxic to aquatic organisms on an acute basis. See Environmental Information.
- There is a potential for workplace exposure to MDI in all industrial, commercial, or manufacturing settings where MDI is present. Dow does not sell MDI for direct consumer use, but it is used as a raw material to make materials that consumers purchase. It is produced, distributed, stored, and consumed in closed systems. See Exposure Potential.
- Contamination of any MDI product with water may have potentially hazardous consequences. At room temperature, water reacts with isocyanates to form both an insoluble urea compound

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and large quantities of carbon dioxide gas. Even relatively small amounts of water can cause significant problems.1 See Physical Hazard Information.

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Manufacture of Product

- **Process** – The manufacture of MDI begins with the condensation of aniline and formaldehyde to form diphenylmethane diamine.

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\text{aniline} + \text{formaldehyde} \rightarrow \text{diphenylmethane diamine} + \text{water}
\]

Subsequent phosgenation yields an aromatic isocyanate product mix largely corresponding to the composition of the polyamine; in the case of the p, p′-diphenylmethane diamine, MDI is obtained.

Typically, a mixture consisting of MDI and its oligomers is produced; (i.e., trimer, hexamer, pentamer and higher adducts). The polyamine adduct, often referred to as polymethylene polyphenylamine (PMPPA), after phosgenation produces polymethylene polyphenyl isocyanate (or polymeric MDI). These polyisocyanates are represented in a simplified manner as follows:

Pure MDI can be recovered via distillation from an MDI/polymeric MDI reaction mixture. Pure 4,4′-MDI is distilled and shipped in molten or frozen form.

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Product Description1,2

Pure MDI is a solid at room temperature, with a melting point of 38°C (100°F). Liquid MDI products (including melted pure, modified and prepolymers) are colorless to yellow liquids with a mild odor. In the United States, MDI is the standard abbreviation for “pure” diphenylmethane disocyanate. The “polymeric” form of MDI (i.e., pMDI) is a brown liquid and typically contains 30 percent to 70 percent of monomeric MDI, with the balance consisting of higher molecular-weight fractions.

MDI is supplied in various forms and products. Most is sold in the form of polymeric MDI. The grades used in rigid-foam production typically contain 30-40% pure MDI, with the balance being other isomers of MDI and their dimers and trimers. Pure MDI is solid at room temperature and is usually supplied in molten form. Only very small quantities of flaked pure MDI are sold.
The Dow Chemical Company (Dow) markets ISONATE™ MDI products, which are sold in both the "pure" form and the "prepolymer" form, and PAPI™ polymeric MDI products, which are sold in the "polymeric" form.

**Product Uses**

MDI-based products are used in applications such as thermoplastic polyurethanes, fibers, sealants, coatings, automotive bumpers, fenders and fascia, integral-skin plastics, tires and wheels, industrial wheels, shoe soles, recreational goods, and mechanical goods. A breakdown of product types and applications based on pure, modified or polymeric MDI follows.

Both pure and modified MDI may be combined with long-chain polyethers, polyesters, or other polyols to produce a wide range of high- and low-density microcellular products and materials (foams), as well as a variety of thermo-plastic polymers suitable for extrusion, injection molding, and solution applications.

Polymeric MDI products are well suited for many industrial, manufacturing, and specialty end-use applications. These applications include insulation for refrigerators and freezers, automotive interior trim and seating, building materials, industrial products, coatings, adhesives, binders, packaging, structural foam, pour-in-place insulation, laminated panel cores, furniture, and bun stock polyisocyanurate.

**Exposure Potential**

MDI is used in the production of industrial and consumer products. A potential user of MDI who plans to work with, handle, or use MDI, or who anticipates coming into contact with MDI in a workplace setting should carefully review the information provided in SDS specific to the particular MDI product involved and should carefully follow the instructions and precautions provided in that SDS.
Based on the uses for MDI, the public could be exposed through:

- **Workplace exposure**
  - There is a potential for workplace exposure to MDI in all industrial, commercial, or manufacturing settings where MDI is present. Such exposure may be harmful if appropriate safe handling and use instructions are not followed, or if appropriate safe handling and use precautions are not employed. For a very general overview of MDI health information, see the section below entitled, “Health Information”.

- **Consumer exposure to products containing MDI**
  - Dow does not sell MDI for direct consumer use, but it is used as a raw material to make materials that consumers purchase. For a very general overview of MDI health information, see the section below entitled, “Health Information”.

- **Environmental releases**
  - If released to the environment, MDI will rapidly react with water to form insoluble polyureas which will tend to float on water and ultimately become associated with soil and sediments. The polyureas will likely be removed in wastewater treatment facilities by association with biosolids. In the event of a spill, the focus is on containing the spill to prevent contamination of soil and surface or ground water. Spills or leaks of MDI should be contained and cleaned up only by properly trained and equipped personnel—all others should leave the contaminated area.

- **Large release**
  - Industrial spills or releases are infrequent and generally contained. If a large spill does occur, the material should be captured, collected, and reprocessed or disposed of according to applicable governmental requirements. Local emergency crews and trained personnel should be called to handle large spills. Only properly trained and equipped personnel should attempt to isolate or contain the spill.

For more information, request the relevant Safety Data Sheet.

**Health Information**

There are many different Dow products that contain MDI. These products are not identical, though they may share similar characteristics and properties. Below are some general statements common to several of the products containing MDI. The statements provided below are not intended to provide all of the health information that may be relevant to each and every MDI product. A potential user of MDI who plans to work with, handle, or use MDI, or who anticipates coming into contact with MDI in a workplace setting should carefully review the information provided in the Safety Data Sheet specific to the particular MDI product involved and should carefully follow the instructions and precautions provided in that SDS.

**Skin contact**
- Skin contact may cause an allergic skin reaction. Animal studies have shown that skin contact with isocyanates may play a role in respiratory sensitization.

**Eye contact**
- MDI may cause moderate eye irritation and slight, temporary corneal injury.

**Inhalation**
- Exposure limits are set by regulatory organizations like the Occupational Safety and Health Administration and other professional organizations like the American Conference of Governmental Industrial Hygienists. Exposure limits typically define the maximum air concentrations to which you can be exposed without the need for respiratory protection. At room temperature, MDI vapors are minimal due to low volatility. However, certain operations may generate vapor or mist concentrations sufficient to cause respiratory irritation and other adverse effects. Such operations include those in which the material is heated, sprayed or otherwise mechanically dispersed such as drumming, venting or pumping. Excessive exposure may cause irritation to upper respiratory tract (nose and throat) and lungs. MDI inhalation exposure may cause pulmonary edema (fluid in the lungs.) Effects may be delayed. Decreased lung function has been associated with overexposure to isocyanates. MDI inhalation above the exposure limits may cause an allergic respiratory response. However, MDI exposure at concentrations below the exposure guidelines may cause allergic respiratory reactions in individuals already sensitized.
Asthma-like symptoms may include coughing, difficult breathing and a feeling of tightness in the chest. Occasionally, breathing difficulties may be life threatening.

**Ingestion** – MDI products have low acute oral toxicity. Small amounts swallowed incidentally as a result of normal handling operations are not likely to cause injury; however, swallowing larger amounts may cause injury.

**Other** – Lung tumors have been observed in laboratory animals exposed to respirable aerosol droplets of MDI/Polymeric MDI for their lifetime. Tumors occurred concurrently with respiratory irritation and lung injury. Current exposure guidelines are expected to protect against these effects reported for MDI. MDI has been toxic to the fetus in laboratory animals at doses toxic to the mother. MDI did not cause birth defects in laboratory animals.

For more information, request the relevant Safety Data Sheet.

**Environmental Information**

Release of MDI to the atmosphere is unlikely, due to its low volatility. In the aquatic and terrestrial environment, MDI reacts rapidly with water, forming insoluble polyureas that are chemically and biologically inert. This reaction limits the movement of MDI in soil and water.

Although the polyureas are non-biodegradable, they are expected to be removed in wastewater treatment facilities by association with biosolids.

Due to their high molecular weight, the polyureas do not accumulate in the food chain and are practically non-toxic to aquatic organisms on an acute basis ($LC_{50}/EC_{50} > 100$ mg/L in the most sensitive species tested).

For more information, request the relevant Safety Data Sheet.

**Physical Hazard Information**

There are several different Dow products that contain MDI. These products are not identical, though they may share similar characteristics and properties. The statements provided below are not intended to provide all of the physical hazard information that may be relevant to each and every MDI product. A potential user of MDI who plans to work with, handle, or use MDI, or who anticipates coming into contact with MDI in a workplace setting should carefully review the information provided in the Safety Data Sheet (SDS) specific to the particular MDI product involved and should carefully follow the instructions and precautions provided in that SDS.

MDI is stable under recommended storage conditions. However, it can decompose at elevated temperatures. Toxic flammable gases and heat are released under decomposition conditions. Generation of gas during decomposition can cause rapid pressure buildup in closed systems.

When working with MDI, contact with acids, alcohols, amines, water, ammonia, bases, metal compounds, moist air, moist organic absorbents and strong oxidizers should be avoided. Diisocyanates like MDI react with many materials and the rate of reaction increases with temperature as well as increased contact; these reactions can become violent. Contact is increased by stirring or if the other material mixes with the diisocyanate.

MDI reacts with water, releasing carbon dioxide and generating heat, which can cause pressure buildup, plugging of lines and valves, and rupture of closed containers. Reaction of MDI with
polyols generates heat. Elevated temperatures accelerate this reaction. Hazardous polymerization can occur at elevated temperatures.

In the presence of oxygen and fire or a heat source sufficient to cause vaporization of the liquid, MDI products will burn. Dense smoke is produced when MDI burns and smoke may contain the original materials in addition to combustion products of varying composition which may be toxic or irritation. Although MDI does not vaporize readily at ambient conditions, explosive limits could be reached under fire conditions.

For more information, request the relevant Safety Data Sheet.

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Regulatory Information

Regulations may exist that govern the manufacture, sale, transportation, use, and/or disposal of MDI. These regulations may vary by city, state, country, or geographic region. Information may be found by consulting the relevant Safety Data Sheet or Contact Us.

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Additional Information

- Safety Data Sheet – ISONATE® Pure MDI Material Safety Data Sheet, The Dow Chemical Company (request using Contact Us at: http://www.dow.com/polyurethane/contact/index.htm)
- Contact Us (http://www.dow.com/polyurethane/contact/index.htm)

For more business information about MDI-based isocyanate products, visit Dow's Polyurethanes web site at http://www.dow.com/polyurethane.

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References

2 ISONATE® Pure MDI Material Safety Data Sheet, The Dow Chemical Company
3 Dow MDI-Based Products, The Dow Chemical Company, Form No. 109-01445-303 EC

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