

PRODUCT SAFETY SUMMARY: MDI, MDI POLYMERS, AND MDI-BASED PRODUCTS

This Product Safety Summary is intended to provide a general description of certain Huntsman chemical substances and products containing the chemical substance(s). The information in this Summary is not intended to replace the information included on the Safety Data Sheet (SDS), Product Safety Label, and other safe use and handling literature for the chemical substance(s).

Chemical Identity

This Product Safety Summary covers a set of methylene diphenyl-diisocyanate chemicals:

CAS #	Chemical Name	Synonyms
101-68-8	4,4'-Diphenylmethane diisocyanate	Methylene diphenyl-diisocyanate, 4,4'-MDI
2536-05-2	Benzene, 1,1'-methylenebis[2-isocyanato-	2,2'-methylenediphenyl diisocyanate, 2,2'-MDI
26447-40-5	Diphenylmethane diisocyanate mixed isomers	methylenediphenyl diisocyanate (generic), MDI
5873-54-1	Benzene, 1-isocyanato-2[(4-isocyanatophenyl)methyl]-	2,4'-Diphenylmethane diisocyanate, 2,4'-MDI
9016-87-9	Isocyanic acid, polymethylenepolyphenylene ester	Diphenylmethane-diisocyanate, isomers and homologues; pMDI; polymeric MDI
32055-14-4	Formaldehyde, oligomeric reaction products with aniline and phosgene	Oligomeric MDI
39310-05-9	Benzene, 1,1'-methylenebis isocyanato, homopolymer	Diphenylmethane diisocyanate homopolymer, MDI homopolymer, MDI homopolymer; Methylenediphenyl diisocyanate, oligomers (Carbodiimid/Uretonimin-type)
123714-19-2	4,4'-Methylenediphenyl diisocyanate, oligomeric reaction products with butane-1,3-diol, 2,4'-diisocyanatodiphenylmethane,	MDI modified with glycols; MDI pre-polymer



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	[(methylethylene)bis(oxy)]dipropanol and propane-1,2-diol	
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General Product Overview

MDI is widely used as a polyurethane component all over the world. Due to its chemical structure, it offers the processing of tailormade materials for a broad variety of applications. It can be used as pure substance, as prepolymers, or in its oligomeric/polymeric form as such or as mixtures.

Polymeric MDI is a mixture of monomeric diisocyanate MDI and higher-molecular-weight forms of MDI that typically are reacted with a polyol to product rigid polyurethane foam. Other MDI-based products also can be reacted with a polyol and/or an amine to form an intermediate material that is used in the production of elastomers, coatings, adhesives, or sealants. MDI-based products may contain varying amounts of this diisocyanate monomer. MDI is a reactive chemical that can irritate the respiratory tract, eyes, and skin. Repeated overexposures or a single large overexposure to airborne MDI above the occupational exposure guideline may cause some people to become sensitized and they may develop diisocyanate asthma.

Specific precautions must be used to minimize exposure and promote safe storage, transport, handling, and use of MDI and MDI-based products. The reaction of diisocyanates with water leads to the formation of insoluble ureas and carbon dioxide gas, which can result in pressure buildup inside closed containers. Extreme care must be taken to avoid atmospheric moisture and water ingress. Containers must be carefully resealed after each sampling.

Applications and Uses

Most MDI and MDI-based products sold by Huntsman are intermediate chemicals used primarily to make rigid and flexible polyurethane foams, such as insulation for your home or refrigerator, mattresses, cushions, and many other uses. MDI and MDI-based products are used in the production of various coatings, adhesives, sealants, and elastomers for items such as paints, glues, and weather-resistant materials. They are also used to make many types of footwear and sports and leisure products, and to produce some specialty flexible foams. MDI and MDI-based products are also used as a binder for wood products, such as particle board, fiberboard, and oriented strand board, among many other uses.

Physical and Chemical Properties

This Product Safety Summary covers a range of MDI products and MDI-based products that have varying physical properties tailored to customer needs. MDI is solid in a flake form, and MDI-based products are typically clear, amber/brown, nonflammable liquids.

An example of the physical properties for polymeric MDI is summarized below:

Boiling point	>300°C
Flash point	>150°C
Vapor pressure	<0.0001 mmHg / <0.001 Pa @ 25°C SDS Rubinate M <0.00001 hPa (20°C)
Density	1.23 g/cm ³ @ 25°C
Solubility in water	Insoluble

Additional physical and chemical property information is available for each MDI and MDI-based product on the product Safety Data Sheet (SDS), which can be requested at SDS@huntsman.com.

Human Health Information

The potential to experience health effects associated with MDI and MDI-based products depends on the exposure level and duration as well as other factors, including individual susceptibility. The potential health effects from exposure to MDI and MDI-based products above the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value-Time Weighted Average (TLV-TWA) or Occupational Safety and Health Administration's permissible exposure limit (OSHA PEL) are discussed below.

Different regulatory classification criteria apply in different geographic regions. These differing criteria can result in different human health regulatory classifications for the same products in different geographic regions. Specific regulatory classification information is contained in the Safety Data Sheet for each product in use in the specific geographic region. The acute and chronic health effects information below is based on Safety Data Sheets in use in the United States.

Acute Health Effects

MDI vapors, aerosols, and mists at concentrations above the ACGIH TLV (8-hour average), OSHA PEL or ACGIH ceiling limit can irritate the mucous membranes in the respiratory tract (nose, throat, lungs), causing runny nose, sore throat, burning sensation, coughing, chest discomfort, shortness of breath and reduced lung function (breathing obstruction).

People with a preexisting, nonspecific bronchial hyperreactivity can respond to concentrations below the TLV or PEL with similar symptoms as well as asthma attacks or asthma-like symptoms. Exposure well above the TLV or PEL may lead to bronchitis, bronchial spasm, and pulmonary edema (fluid in lungs). Chemical or hypersensitivity pneumonitis, with flu-like symptoms (e.g., fever, chills), has also been reported. These symptoms can be delayed up to several hours after exposure. These effects are usually reversible.

MDI skin exposure may cause irritation with symptoms of reddening, itching, and swelling. People previously sensitized can experience allergic skin reaction with symptoms of reddening, itching, swelling, and rash. Contact with MDI can cause skin discoloration.

MDI may cause eye irritation with symptoms of reddening, tearing, stinging, and swelling. Direct eye exposure may cause temporary corneal injury. Vapor or aerosol may cause irritation with symptoms of burning and tearing.

MDI ingestion may cause irritation; symptoms may include abdominal pain, nausea, vomiting, and diarrhea.

Chronic Health Effects

As a result of repeated inhalation overexposures or a single large dose, some people may develop sensitization to MDI or other diisocyanates. Once sensitized, a person can react to later diisocyanate exposures at levels well below the TLV or PEL exposure limits, resulting in asthma or asthma-like symptoms. These symptoms, which can include chest tightness, wheezing, cough, shortness of breath, or asthmatic attack, could be immediate or delayed up to several hours after exposure. Extreme asthmatic reactions can be life threatening.

There are reports that once sensitized, a person can experience these symptoms upon exposure to dust, cold air, or other irritants, which is a non-specific asthmatic response. This increased lung sensitivity can persist for weeks or, in severe cases, several years. Sensitization can be permanent. Chronic overexposure to diisocyanates has also been reported to cause lung damage (including fibrosis and/or decrease in lung function) that may be permanent.

Prolonged skin contact can cause reddening, swelling, rash, and, in some cases, skin sensitization. Animal tests indicate that skin contact with MDI may play a role in causing



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respiratory sensitization. This data reinforces the need to prevent direct skin contact with isocyanates.

Prolonged vapor contact may cause conjunctivitis.

In chronic two-year carcinogenicity studies, animals exposed to MDI at concentrations that significantly exceed workplace exposure guidelines experienced a slight increase in tumor formation in the respiratory tract (site of contact). Tumor formation in the animal studies was only associated with excessive, prolonged irritation to aerosols in a form and concentration unlikely to be formed in a workplace environment. Thus, tumor formation in the workplace is highly unlikely. This conclusion is supported by multiple industrial cohort studies for up to 40 years that found no association of occupational exposure to MDI and increased risk of cancer formation.

The mutagenic effect of MDI was tested and showed positive and negative results in various tests. However, properly conducted confirmatory studies lead to the overall conclusion that, based on a weight of evidence assessment, MDI and MDI-based products are not mutagenic.

Animal experiments showed no indication of specific developmental toxicity. Indirect evidence did not indicate a potential for reproductive toxicity.

More information can be obtained in the specific product Safety Data Sheet, which can be requested at SDS@huntsman.com.

Environmental Information

Environmental Fate

Due to their reactivity, MDI and MDI-based products are manufactured and handled in water-free processes and in closed systems. During normal operating conditions, MDI and MDI-based products are not expected to be released to the air, soil, or water. Procedural and/or control technologies are used to minimize emissions and potential exposure during cleaning and maintenance activities.

If there is an unintentional release, MDI is not rapidly biodegradable but is not expected to bioaccumulate and will hydrolyze in water. Hydrolysis is the dominant process in determining the overall environmental fate of MDI and MDI-based products and the main removal mechanism of MDIs in the environment. Hydrolysis half-lives of polymeric MDI constituents have been measured in the range of 18 to 24 hours. MDI and MDI-based products have low vapor pressures and releases via air are unlikely. Half-life in air is expected to be approximately 1 day (0.92d). Supportable data on the bioaccumulation of



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MDI and MDI-based products are available, indicating a low potential for bioaccumulation in the environment. MDI and MDI-based products will react with water to form CO² and a solid material (polyurea), which is insoluble and inert. Due to the MDI reactivity, no significant accumulation and/or transport in environmental media is expected.

Environmental Toxicity Testing

Environmental toxicity test data from several aquatic species show that MDI and MDI-based products have low to moderate environmental toxicity. There is no indication that the MDI and MDI-based products are expected to show toxicity towards terrestrial organisms.

More information can be obtained in the product Safety Data Sheet.

Potential Occupational Exposure

Many MDI and MDI-based products are manufactured in closed systems. During normal operating conditions, occupational exposure to MDI and MDI-based products is not expected in the manufacturing process. Procedural and/or control technologies are used to minimize exposure during sampling, cleaning, maintenance, upset conditions, or in more open manufacturing systems. In those cases, prescribed personal protective equipment is required.

Industrial and professional applications of MDI and MDI-based products where the product is heated or sprayed may result in the potential exposure of workers. Users of those products should conduct air sampling and use appropriate engineering controls (i.e., ventilation) and personal protective equipment according to the exposure guidelines and workplace practices identified in the product Safety Data Sheet.

Potential Consumer Exposure

Most MDI-based products are not sold for consumer use but instead are sold to industrial or commercial customers that react or further process the products for end-use applications. When the end-use products are used as intended, they are not expected to present an exposure risk to consumers. Some MDI-based products are not reacted for end-use applications but are formulated by commercial customers for resale to consumers, and when used as intended, are not expected to present an exposure risk to consumers. Fully cured products are fully reacted



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and therefore “are considered to be inert and non-toxic” by the United States Environmental Protection Agency (EPA).¹

Safe Use Recommendations/Workplace Exposure Controls

Huntsman follows and recommends that customers follow workplace exposure guidelines through a variety of industrial hygiene and ventilation measures. Workplace exposure guidelines include workplace limit values:

- TLV-TWA (the concentration for a conventional 8-hour workday and a 40-hour workweek for a working lifetime without adverse effect) of 0.005 ppm for 4,4'-MDI
- A ceiling limit (the concentration that should not be exceeded during any part of the working exposure) of 0.02 ppm for 4,4'-MDI

Several validated sampling and analytical methods are available to evaluate potential exposures to airborne MDI. Further, during certain handling and use conditions with inadequate ventilation when MDI is sprayed, aerosolized or heated, airborne concentrations can exceed the appropriate standard/guideline. In these instances, respiratory protection is required. In addition, appropriate skin and eye protective equipment should be worn to prevent contact with MDI.

Because of the possibility of sensitization, employees who are assigned to an isocyanate work area should undergo a pre-placement medical evaluation and be part of a comprehensive medical surveillance program. Once a worker has been diagnosed as sensitized to any isocyanate, no further isocyanate exposure should be permitted.

See the Safety Data Sheets for MDI and specific MDI-based products for additional information about first aid measures, accidental releases (spills and leaks), waste disposal, toxicity, transportation, regulatory requirements and other important topics.

Regulatory Information/Classification and Labeling

Under the Globally Harmonized System (GHS) for Hazard Communication, substances are classified according to their physical, health, and environmental hazards. The hazards are communicated via specific labels and the Safety Data Sheets. GHS attempts to standardize

¹ Methylene Diphenyl Diisocyanate (MDI) And Related Compounds Action Plan [RIN 2070-ZA15] (Tech.). (2011). Washington, DC: U.S. Environmental Protection Agency. Retrieved March 20, 2019, from <https://www.epa.gov/sites/production/files/2015-09/documents/mdi.pdf>.

hazard communication so that the intended audience (workers, consumers, transport workers, and emergency responders) can better understand the hazards of the chemicals in use.

Note: The hazard statements and symbols presented here refer to the hazard properties of the concentrated substance and are meant to provide a brief overview of the substance's labeling. It is not intended to be comprehensive or to replace information found in the Safety Data Sheet.

Labeling according to OSHA 1910.1200 (GHS)



Signal Word

Danger

GHS Classification	
Acute toxicity (inhalation)	Category 4
Skin irritation	Category 2
Eye irritation	Category 2B
Respiratory sensitization	Category 1
Skin sensitization	Category 1
Specific target organ toxicity – single exposure	Category 3 (respiratory system)

Hazard Statements	
H315 + H320	Causes skin and eye irritation
H317	May cause an allergic skin reaction
H332	Harmful if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H335	May cause respiratory irritation



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Additional Information

Information on registered substances is available on the European Chemicals Agency (ECHA) website at <https://echa.europa.eu>.

Most commonly used synonyms

Benzene, 1,1'-methylenebis [4-isocyanato-, homopolymer]

References

- Center for Polyurethanes Industry website: <https://polyurethane.americanchemistry.com>
- American Chemistry Council Diisocyanates Panel website: <https://dii.americanchemistry.com>



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