Product Safety Assessment

*DOW™ Modified Methyl Diphenyl Diisocyanate (MDI) Products*


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**Names**

- CAS No. 26447-40-5 (Generic MDI)
- CAS No. 9016-87-9 (Polymeric MDI)
- CAS No. 101-68-8 (4,4’-Methylenebisphenol diisocyanate)
- Methylene diphenyl diisocyanate (MDI)
- 1,1’-Methylenebis[4-isocyanatobenzene]
- Modified MDI
- MDI products
- MDI formulations
- MDI prepolymer
- MDI variants

Tradenames for DOW™ modified MDI products include, but are not limited to:

- AUTOTHANE™ prepolymer
- DELTA-THERM™ isocyanates
- DIPRANE™ isocyanates and prepolymer
- DUOTHANE™ prepolymer
- DURAMOULD™ prepolymer
- DURELAST™ isocyanates
- DYNATHANE™ isocyanates and prepolymer
- ENFORCER™ isocyanates
- ENHANCER™ isocyanates
- HYPERCRETE™ prepolymer
- HYPERKOTE™ isocyanates and prepolymer
- HYPERLAST™ isocyanates and prepolymer
- HYPOL™ isocyanates and prepolymer
- ROTAKOTE™ prepolymer
- SPECFIL™ isocyanates
- SPECFLEX™ isocyanates
- SPECTRIM™ isocyanates
- TRAFFIDECK™ isocyanates and prepolymer
- VORACOR™ isocyanates
- VORALAST™ isocyanates
- VORALUX™ isocyanates
- VORAMER™ isocyanates
- VORASTAR™ isocyanates
- VORATEC™ isocyanates
- VORATRON™ isocyanates
- XiTRACK™ isocyanates

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Product Overview

- This product assessment covers a group of products that share similar chemistry and properties. For detailed information, refer to each product’s Material Safety Data Sheet (MSDS) also called Safety Data Sheet (SDS).
- MDI is the abbreviation for methylene diphenyl diisocyanate. DOW™ modified MDI products are made by reacting MDI with materials that have hydroxyl (-OH) groups. Modified MDI products are also called MDI variants. DOW modified MDI products are produced by Dow Polyurethane Systems and Dow Hyperlast, businesses of The Dow Chemical Company (Dow). For further details, see Manufacture of Product.
- DOW modified MDI products are used in customized formulations or blends of chemicals designed for a specific application. These materials always contain some free or unreacted MDI. For information on pure and polymeric MDI, read Dow's Product Safety Assessment MDI-Based Isocyanate Products. Modified MDI products are yellow to brown colored, highly-reactive liquids or semi-solids. Dow markets modified MDI products under different tradenames based on end-use market applications. For this document, the term “modified MDI products” includes MDI-based prepolymer products as well as MDI-based formulations. Many modified MDI products contain additives such as toluene diisocyanate (TDI), foam blowing agents, flame retardants, surfactants, colorants, and plasticizers. For further details, see Product Description.
- Modified MDI products are chemical intermediates or raw materials used for the manufacture of polyurethane foams, elastomers, coatings, adhesives, and binders. These products are used in applications ranging from appliances, furniture and shoes, to decorative molding, boats, automobiles, and athletic equipment. For further details, see Product Uses.
- There is a potential for workplace exposure to MDI in all industrial, commercial, or manufacturing settings where MDI is present. Each manufacturing facility should have a thorough training program for employees, appropriate work processes and safety equipment in place to limit unnecessary exposure. Dow does not sell MDI for direct consumer use, but it is used as a raw material to make materials that consumers purchase. For further details, see Exposure Potential.
- MDI is a highly reactive hazardous chemical 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. Modified MDI products may also contain additives that have additional health risks. Users of these materials should carefully review and follow the instructions and precautions provided in each product’s Safety Data Sheet (SDS). For further details, see Health Information.
- DOW modified MDI products will rapidly react with water in the environment to form insoluble polyurea solids. These polyureas are generally not biodegradable and are resistant to hydrolysis (i.e. inert), are unlikely to accumulate in the food chain, and are practically non-toxic to fish and other aquatic organisms. For further details, see Environmental Information.
- FOR EMERGENCY RESPONSE INSIDE THE UNITED STATES: Call CHEMTREC (1-800-424-9300) for advice on spilled MDI products, fire, or other handling issues. Modified MDI products are highly reactive liquids that can only be handled by trained individuals. These materials react with water to produce heat and carbon dioxide (CO₂) gas. For further details, see Physical Hazard Information.

Manufacture of Product

- Capacity – In 2008, worldwide production capacity for MDI-based diisocyanates and polyisocyanates was 5,260 metric kilotonnes (about 11.6 billion pounds). Dow is one of the major producers of MDI and modified MDI products. Dow is one of four major MDI manufacturers in the U.S. Dow’s global capacity for MDI-based diisocyanates and polyisocyanates is 553 metric kilotonnes (over 1.2 billion pounds) from facilities in the U.S.,

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Germany, Portugal, Japan, and Korea. DOW™ modified MDI products are produced by Dow Polyurethane Systems and Dow Hyperlast. Dow’s Systems businesses operate a global network of 26 system houses.

- **Process** – For information about the production of MDI, see *Product Safety Assessment MDI-Based Isocyanate Products*. DOW™ modified MDI products and prepolymer are manufactured by carefully controlled reactions between MDI and hydroxyl-containing materials. If the number of hydroxyl groups is lower than the number of isocyanate groups, a modified MDI prepolymer is formed. A simplified reaction between MDI and a diol (a dihydroxy material) is shown below.

![Modified MDI Product, also called MDI Variant](image)

**Product Description**

MDI is the standard abbreviation for methylene diphenyl diisocyanate. "MDI" refers to a mixture of 4,4'-methylene diphenyl diisocyanate and its isomers.

DOW™ modified MDI products are industrial chemicals manufactured from MDI and are customized formulations or blends of chemicals designed for a specific application. Modified MDI products are prepared by reacting MDI’s isocyanate groups (–N=C=O) with polyols that have hydroxyl (–OH) groups. These materials are manufactured and formulated according to customer specifications and end-use applications. To tailor the product properties, components may be added to the reaction process. Additives may include foam blowing agents, flame retardants, surfactants, colorants, and plasticizers. All modified MDI products contain some free or unreacted MDI.

DOW modified MDI products are liquids or semi-solids that vary in color from yellow to amber to brown, with musty to mild odors depending on the nature of the polyol, the amount of free MDI, and other components or additives that are present. Dow markets these products under different tradenames for different end-use market applications.

Dow tradenames for modified MDI products include but are not limited to:

- AUTOTHANE™ prepolymer
- DELTA-THERM™ isocyanates
- DIPRANE™ isocyanates and prepolymer
- DUOTHANE™ prepolymer
- DURAMOULD™ prepolymer
- DURELAST™ isocyanates
- DYNATHANE™ isocyanates and prepolymer
- HYPOL™ isocyanates and prepolymer
- ROTAKOTE™ prepolymer
- SPECFIL™ isocyanates
- SPECFLEX™ isocyanates
- SPECTRIM™ isocyanates
- TRAFFIDECK™ isocyanates and prepolymer
- VORACOR™ isocyanates

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- ENFORCER™ isocyanates
- ENHANCER™ isocyanates
- HYPERCRETE™ prepolymers
- HYPERKOTE™ isocyanates and prepolymers
- HYPERLAST™ isocyanates and prepolymers
- VORALAST™ isocyanates
- VORALUX™ isocyanates
- VORAMER™ isocyanates
- VORASTAR™ isocyanates
- Voratec™ isocyanates
- XiTRACK™ isocyanates

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**Product Uses**

MDI is commonly used to manufacture the following types of polyurethane foams:
- Rigid and semi-rigid
- Flexible
- Integral skin
- Microcellular

MDI is also used to make:
- Elastomers
- Coatings
- Adhesives
- Binders

These products are used in applications ranging from appliances, furniture, and shoes, to decorative molding, boats, and athletic equipment.

DOW™ modified MDI products are used to produce polyurethanes for the following applications:
- AUTOTHANE™ prepolymers – microcellular elastomers for impact, shock, and vibration management in vehicle suspensions and chassis
- DELTA-THERM™ isocyanates – mining, civil engineering, and pipeline construction
- DIPRANE™ isocyanates and prepolymers – durable and solvent-resistant elastomers
- DUOTHANE™ prepolymers – sealants, caulking, adhesives, gaskets, wear pads, structural parts
- DURAMOULD™ isocyanates – cast concrete, rapid prototyping, and tooling industries
- DURELAST™ isocyanates – furniture edgings
- DYNATHANE™ isocyanates and prepolymers – elastomers that reduce vibration and noise
- ENFORCER™ and ENHANCER™ isocyanates – carpet backing
- HYPERKOTE™ isocyanates – protective coatings designed for industrial and automotive use
- HYPERLAST™ isocyanates – general elastomers for material handling and industrial engineering
- HYPOL™ prepolymers – hydrophilic polyurethane foams, elastomers, coatings, adhesives, or gels
- ROTAKOTE™ prepolymers – elastomers for rotational coatings
- SPECFIL™ isocyanates – widely used by the automotive industry for filter gasketing (oil, fuel and air), for the production of industrial filters, for in-situ gasketing applications, climate control systems, ventilation systems, and as dust filters in respiration masks
- SPECFLEx™ isocyanates – flexible and integral skin foams used in the furniture and transportation industries for steering wheels, automotive seating, headrests, and dashboards
- SPECTRIM™ isocyanates – reaction moldable products for the transportation industry such as bumpers, rocker panels, spoilers, and grills

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2008 U.S. Consumption of MDI

- Microcellular: 3%
- Cast Elastomers: 3%
- Thermoplastic Elastomers: 3%
- Rigid Foam: 60%
- Flexible Foam: 12%
- Binders: 14%
- Adhesives & Sealants: 5%
• TRAFFIDECK™ isocyanates and prepolymer – waterproofing and surfacing systems for parking decks, roofs and balconies, bridges, and marine use
• VORACOR™ isocyanates – rigid foam insulation for the construction industry, commercial refrigerators, water heaters, pipeline insulation, roofing, manufactured housing and modular construction
• VORALAST™ isocyanates – lightweight expanded microcellular foam for any type of footwear soling such as sandals, slippers, and midsoles for sport shoes
• VORALUX™ isocyanates – high-resilience foam for furniture and automotive pillars
• VORAMER™ isocyanates – adhesives and binders in a variety of recycling applications, bonding together different kinds of shredded materials such as rubber, flexible polyurethane foams, ethylene-vinyl acetate (EVA), cork and gravel
• VORASTAR™ isocyanates – elastomers used for the furniture and decorative industries; coatings, adhesives, sealants, and elastomers (CASE); mining and transportation industries
• VORATEC™ isocyanates – expanded rigid foams used for commercial refrigerators, freezers, water heaters, portable appliances, and prefabricated panels
• VORATRON™ isocyanates – elastomers and casting resins for electronics and electrical insulation
• XITRACK™ isocyanates – rail stabilization through treatments that improve track quality

Exposure Potential

Modified MDI products are 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 the Safety Data Sheet specific to the particular MDI product involved and should carefully follow the instructions and precautions provided in that Safety Data Sheet.

Based on the uses for these products, 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 Health Information.

• **Consumer exposure to products containing DOW™ modified MDI products** – Polyurethane Systems and Dow Hyperlast products are for industrial use only. Consumers may purchase goods that have been manufactured with modified MDI products; however, by the time these goods reach the consumer, the polyurethane has fully cured (hardened) and risk of exposure to unreacted MDI is very low. See Health Information.

• **Environmental releases** – All spills and leaks should be immediately contained to prevent contamination of soil, 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. Environmental emissions of DOW modified MDI products are unlikely to result from their manufacture and/or intended use, as contact of these products with air, water, or soil results in reactions which degrade product purity and performance. For more information, see the section below entitled, “Environmental Information.”

• **Large release** – Industrial spills or releases are infrequent and are 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.

• **In case of fire** – Keep people away. Isolate fire and deny unnecessary entry. Stay upwind and out of low areas where gases can accumulate. Water is not recommended but may be...
applied in large quantities as a fine spray when other extinguishing agents are not available. Use water fog or fine spray, dry-chemical or carbon-dioxide extinguishers, or foam to fight the fire. Alcohol-resistant foams are preferred. A direct water stream may spread the fire. Consider the use of unmanned hose holders or monitor nozzles. Firefighters should wear positive-pressure, self-contained breathing apparatus (SCBA) with an approved full-face mask and protective firefighting clothing. Contain fire water run-off if possible. Fire water run-off, if not contained, may cause environmental damage. Follow emergency procedures carefully.

For more information, see the relevant Safety Data Sheet or the ISONATE™ and PAPI™ Pure, Modified and Polymeric MDI Safe Handling and Storage Guide.

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Health Information

Health information for DOW™ modified MDI products is summarized on the relevant Safety Data Sheets. A potential user of modified MDI products who plans to work with, handle, or use modified MDI products, or who anticipates coming into contact with modified MDI products in a workplace setting should carefully review the information provided in the Material Safety Datasheet specific to the particular modified MDI product involved and should carefully follow the instructions and precautions provided in that MSDS. It is important to note that health risks associated with individual products may vary based on their formulation or intended use. All modified MDI products contain some free or unreacted MDI. They may also contain minor components or additives that have additional health risks. The Safety Data Sheet is the preferred source for specific health information. An overview of MDI health information appears below.

**Eye contact** – MDI may cause moderate eye irritation and slight, temporary corneal injury. Chemical goggles should be used when working with MDI products and an eye wash fountain should be located in the immediate work area.

**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.

**Inhalation** – 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 the 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.

**Respiratory sensitization** – MDI inhalation may cause an allergic respiratory response. MDI 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 has 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. Good personal hygiene practices must be observed and hands washed before eating. Food should not be stored or consumed where MDI is used.

**Other** – Lung tumors have been observed in laboratory animals exposed to respirable aerosol droplets of MDI/polymeric MDI (6 mg/m³) aerosols for their lifetime. Tumors occurred concurrently

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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, see the relevant Safety Data Sheet.

Environmental Information\textsuperscript{17,18}

Spilled MDI and modified MDI products should be prevented from entering into soil, ditches, sewers, waterways and/or groundwater. Environmental risks associated with individual DOW™ modified MDI products vary by formulation and application. The Safety Data Sheet is the preferred source for specific information. All modified MDI products contain some free or unreacted MDI. An overview of general environmental information for MDI and modified MDI products appears below.

MDI and modified MDI products are insoluble in water and have low vapor pressure. Upon contact with water or moist air, the products will react to form stable, insoluble polyurea solids. This reaction dramatically limits the mobility of these products in the event of a spill (spills are localized and have only transient impact), and the products will tend to remain in and react within the environment to which they are released.

Due to their low vapor pressures, emissions of MDI and modified MDI vapor to the atmosphere are unlikely. In the event vapors are released, MDI is expected to degrade rapidly.

The polyurea solids formed by reaction of MDI and modified MDI products with water have been shown to be resistant to biodegradation and hydrolysis. However, they are also practically non-toxic and will not accumulate in the food chain. They are thus regarded as “inert” in the environment. Trace amounts of minor water-soluble products of the reaction of pure MDI substances with water have been shown to be slightly to practically non-toxic to a number of aquatic species in both short- and long-term tests.

For more information, see the relevant Safety Data Sheet.

Physical Hazard Information\textsuperscript{19,20}

It is important to note that the physical hazard risks associated with individual DOW™ modified MDI products may vary by formulation and application. The Safety Data Sheet is the preferred source for specific physical hazard information. All modified MDI products contain some free or unreacted MDI. An overview of MDI physical hazard information appears below.

MDI is stable under recommended storage conditions. However, it can decompose at elevated temperatures. Gas generated during decomposition can cause pressure in closed systems. Pressure build up can be rapid. MDI reacts with water, releasing carbon dioxide gas. The resulting pressure build up can cause closed containers to rupture. Elevated temperatures can accelerate this reaction.

MDI can react with many materials and release heat. Avoid contact with acids, alcohols, amines, water, ammonia, bases, metal compounds, strong oxidizers, and moist air.

During a fire, smoke may contain MDI in addition to toxic and/or irritating compounds. Hazardous combustion products may include, but are not limited to: nitrogen oxides, isocyanates, carbon monoxide, carbon dioxide and hydrogen cyanide.
Hazardous polymerization of MDI can occur. Polymerization can be catalyzed by strong bases and water.

For more information, see the relevant Safety Data Sheet or the ISONATE™ and PAPI™ Pure, Modified and Polymeric MDI Safe Handling and Storage Guide.

Regulatory Information

Regulations may exist that govern the manufacture, sale, transportation, use and/or disposal of DOW™ modified MDI products. 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.

Additional Information

- Safety Data Sheet – (Request from the Dow Customer Information Group: http://www.dow.com/assistance/dowcig.htm)
- Contact Us (http://www.dow.com/pusystems/contact/index.htm)
- U.S. Environmental Protection Agency Integrated Risk Information System (IRIS) website – Methylene Diphenyl Diisocyanate (monomeric MDI) and polymeric MDI (PMDI) (CASRN 101-68-8, 9016-87-9): (http://www.epa.gov/NCEA/iris/subst/0529.htm)
- U.S. EPA Technology Transfer Network Air Toxics website – 4,4-Methylene diphenyl diisocyanate (MDI), Hazard Summary—Created in April 1992, Revised January 2000: (http://www.epa.gov/ttn/latw/hlthef/methyl-d.html#ref5)

For more business information about DOW™ modified MDI products, visit:
- Dow’s Polyurethane Systems website at www.dow.com/pusystems
- Dow’s Hyperlast website at www.dow.com/hyperlast/index.htm
- Dow’s Polyurethanes website at www.dow.com/polyurethane

References


7 Dow Polyurethane Systems website – About Us: (http://www.dow.com/pusystems/about/index.htm).


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