Product Safety Summary
Diphenylmethane Diisocyanate

This Product Safety Summary is intended to provide a general overview of the chemical substance. The information on the Summary is basic information and is not intended to provide emergency response information, medical information or treatment information. The summary should not be used to provide in-depth safety and health information. In-depth safety and health information can be found on the Material Safety Data Sheet (MSDS) for the chemical substance.

Chemical Identity

Abbreviation:	MDI
CAS Number :	5873-54-1 for 2,4'-MDI 101-68-8 for 4,4'-MDI 2536-05-2 for 2,2'-MDI 9016-87-9 for polymeric MDI 26447-40-5 for non-isomer specific
Common Names:	2, 4-Diphenylmethane diisocyanate Aromatic Diisocyanate Methylene bisphenyl isocyanate Lupranate®, Lupranat®

Product Overview

- Diphenylmethane Diisocyanate, (MDI) is a reactive material. Reactions of the reactive site of MDI (N=C=O) with polyol (-OH) functional materials produce polyurethane compounds.
- BASF's trademarks for MDI are Lupranate® (North America) and Lupranat® (Europe).
- MDI (diphenylmethane diisocyanate) and its different modified forms are reactive chemicals which may be supplied as a liquid or solid. In combination with polyols (polyesters, polyethers), they are used for the manufacture of cellular (foamed) and non-cellular (compact) PUR polymers including coatings, elastomers, adhesives, textiles, and paints.
- MDI in its many forms is widely used in a range of markets such as automotive, furniture, construction, appliances, insulation, and recreation.
- MDI is available in three broad types of compositions:
  - Polymeric MDI (PMDI)
  - Monomeric MDI (MMDI)
  - Modified MDI
- PMDI's principal use is in rigid foam insulation for the construction and refrigeration industries. It is also used in producing high resilience flexible, semi-rigid and packaging polyurethane foams and in a number of non-foam applications such as carpet backing, adhesives, composite wood binder, plywood patching compounds, and foundry core binders.
- MMDI is used in a multitude of thermoplastic and cast elastomer applications, and is the starting material for a variety of modified MDI products. It is also used to prepare coatings, adhesives, sealants, and synthetic fibers.

- Modified MDIs are used in producing reaction injection molded (RIM) polyurethane automotive body parts, microcellular elastomers, integral skin foams, flexible foams, adhesives, coatings, and sealants.
- Like any reactive chemicals, MDI products can create hazards if handled carelessly. All persons associated with the transportation, storage or handling of MDI (or products containing MDI) must understand their hazards. This includes training in the recommended normal and emergency handling procedures.
- The primary hazard with MDI is the inhalation of its vapors. Airborne limits have been established for MDI vapor concentrations in the work environment. See Occupational Health and Safety Administration (OSHA) and American Conference of Governmental Industrial Hygienists (ACGIH) guidelines for these levels. Exposure to MDI may also cause skin irritation or even sensitization from exposure. Animal skin exposure has lead to respiratory sensitization, however it is unknown what the effect is in humans
- For further safety and health information, the current Material Safety Data Sheet (MSDS) should be used for this substance.

Physical/Chemical Properties

- Polymeric MDI (PMDI) is a brownish liquid. It is a mixture of MDI (4, 4'-) and other MDI isomers (2, 4'-, 2, 2'-) and higher molecular weight oligomers. PMDI starts to decompose at temperatures above 230°C [446°F with the evolution of carbon dioxide (CO_2)]. At 25°C (77°F), it has a low vapor pressure of 10^{-5} mbar ($7.5X10^{-6}$ mm HG).
- Monomeric MDI (MMDI) is a white to yellowish solid or liquid. It consists of over 97% 4, 4'-MDI with small amounts of 2, 4'-MDI and traces of the 2, 2'-isomer. It is a solid with a melting point of about 38.5°C (101.3°F), and a boiling point of 210°C (410°F) at 7 mbar (5 mm Hg). It starts to decompose at about 230°C (446°F). At 25°C (77°F), it has a low vapor pressure of 10-5 mbar ($7.5X10^{-6}$ mm Hg).
- Modified MDI varies in color and are chemically tailored to the requirements of specific applications and processes.
- The specific gravity of MDI ranges from 1.20 to 1.23, depending on type. MDI is denser than water and will sink to the bottom of water-filled containers.
- MDI reacts with water and can generate heat, however the reaction depends on temperature. If the temperature is below 50°C then the reaction is slow and at higher temperatures above 50°C the reaction becomes progressively more vigorous and can be violent. The reaction of MDI with water forms both carbon dioxide (CO_2) and insoluble polyurea compounds.
- MDI will also react with basic materials such as sodium hydroxide, ammonia, primary and secondary amines, acids and alcohols. Reaction with some of these products may be violent, generating heat, which can result in an increased evolution of MDI vapor and the formation of CO_2.

Health Information

Acute Hazards

MDI and products containing unreacted MDI are potentially hazardous materials. A thorough knowledge of potential dangers, with strict adherence to recommended safety practices, is essential before MDI products are handled, stored or used. Workers must be properly instructed and supervised in the handling of MDI. MDI can be potentially hazardous in liquid, vapor, mist (aerosol), or dust form. Aerosols are airborne droplets and maybe present anywhere MDI is sprayed. These droplets may present a risk even at normal temperatures. A dust hazard may arise whenever solid MMDI or MDI is absorbed

on finely divided materials when handled. The primary hazard with MDI is the inhalation of its vapors. Limits have been established for allowable MDI vapor concentrations in the work environment. The OSHA permissible exposure limits (PEL) for MDI is 0.005 ppm as an 8-hour time weighted average (TWA) concentration and as a ceiling concentration limit of 0.02 ppm.

Effects on Respiratory System:
High concentrations (above the Occupational Exposure Limit) of MDI vapor, aerosol, or dust may irritate the mucous membranes of the nose, throat, and lungs. It may cause throat dryness and tightness in the chest and breathing difficulties. Overexposure symptoms may be delayed. Allergic reactions can appear in susceptible persons. The health of all personnel coming into contact with MDI should be regularly monitored.

Effects on Eyes:
Direct eye contact with MDI products may produce severe watering, irritation and inflammation of mucous membranes. Corneal opacity and discharge may result, if MDI is not removed.

Effects on Skin:
Skin contact with MDI may result in irritation and a mild tanning action, depending on the amount and length of contact. Direct contact may produce skin sensitization, contact dermatitis, and eczema from repeated exposure. An animal study indicates that MDI may induce respiratory hypersensitivity upon dermal exposure.

Effects on Ingestion:
The effects of ingestion include irritation and burning of the mouth, esophagus, and stomach. The LD_{50} (oral-rat) for MDI is greater than 5000 mg/kg.

Chronic Hazards
Repeated exposure of the skin, the eyes, nose or upper respiratory tract may cause chronic irritation.

Some individuals may develop a hypersensitivity to MDI vapors and may experience a severe reaction when exposed to MDI vapors at concentrations below established guidelines. Symptoms of hypersensitivity to MDI may include wheezing, shortness of breath and difficulty in breathing (See Sensitization). Long-term overexposure to diisocyanates has also been reported to cause lung damage, including reduced lung function, which may be permanent. Exposure above the PEL may result in bronchitis, bronchial spasms and pulmonary edema. Long-term exposure to MDI has been reported to cause lung damage including reduced lung function that may be permanent.

Sensitization
Sensitization is an affect whereby a physiological response is caused by re-exposure to a very low concentration of chemical in an individual following higher, initial acute exposure or following chronic exposures. The response may be immediate, delayed or both.

The PEL values and ceiling limits should be sufficiently low to prevent sensitization in most individuals. However, allergic reactions may occur in sensitized individuals at concentrations well below these values. Once sensitized, individuals should be excluded from further exposure. If sensitized individuals continue to work with MDI, the time period between exposure and onset of symptoms may be shortened and the severity of the symptoms may increase.

To determination of what constitutes a significant MDI exposure can be difficult. The minimum concentration of MDI in the atmosphere that will cause subjective symptoms and objective physical findings in any given individual is unknown. Responses in sensitized individuals vary considerably from one individual to another.

Environmental Information

Any release to the environment of over 5000 lbs. must be reported to the NRC and the local planning commission as outlined under EPCRA regulations. Each plant should have a system for dealing with emergencies within the plant to limit environmental release.

MDI will react with water to form carbon dioxide (CO_2) and insoluble polyurea compounds, which are not biodegradable but chemically inert. Because of this reaction, all unreactive MDI release to the environment would be consumed when exposed to water, water in the air or water in the ground.

Environmental toxicity test data from several animal species shows that MDI is practically nontoxic or not appreciably toxic to animals.

Additional Hazard Information

The reaction of MDI with moisture, even from ambient air, will produce polyurea solids and CO_2 gas. These insoluble polyureas will deposit on surfaces of pipes and tanks causing line restrictions and filtration problems. The generated CO_2 could present a pressure hazard, including the potential of a violent rupture of an under-vented tank or vessel.

Although MDI is relatively non-flammable (flash point 200°/392°F), MDI should not be stored adjacent to highly flammable materials. Water, dry chemical, protein foam, or CO_2 fire extinguishers should be available in all storage and processing areas. Automatic fire or smoke detection equipment as well as automatic sprinklers should be installed in all MDI processing and storage areas.

Polymeric MDI (PMDI) - To maintain product quality, it is important that polymeric MDI products must be stored and handled correctly. It is imperative that polymeric MDI products be stored under dry conditions. Storage tanks should be maintained under positive pressure pads with dry air or dry nitrogen[1] the storage temperature will affect the handling characteristics and product quality of the polymeric isocyanates. The most favorable temperature for storage is 20 to 30°C (68 to 86°F). The recommended storage temperatures for specific polymeric MDIs from BASF are also reported in our Technical Leaflets or Technical Bulletins.

Monomeric MDI (MMDI) - MMDI will degrade quickly unless it is stored and handled correctly. Excess dimer formation will result in turbidity or the precipitation of dimer solids in the liquid. The optimum storage condition for solid MMDI is as cold as possible (e.g., <0°C/<32°F). Below this temperature, the rate of dimer formation is minimized. If it is kept under dry air or dry nitrogen, the product may be stored up to three months after date of manufacture without a change in properties. If MMDI is stored as a solid, melting for use is best accomplished by rolling the drum in a hot air oven at 80 to 100°C (176 to 212°F). The drum contents should not be heated above 70°C (158°F) to minimize dimer formation. Heating by electrical means is not recommended due to the danger of local overheating. Melting MMDI in a water bath or with steam is likewise not recommended because of the potential danger of drum leakage. When MMDI is to be stored or processed as a

[1] Dry air or nitrogen should have a dew point below –40°C (-40°F).

liquid, the optimum temperature for storage is between 40 and 44°C (104 and 111°F). Liquid MMDI when stored with a dry nitrogen blanket will retain its properties for up to 14 days. If the product is kept outside this range, it will degrade quickly. The rate of dimer formation is greatest near the melting point (38°C/100°F) for the solid, and above 50°C (122°F), for the liquid. Liquid MMDI must be stored under dry nitrogen because contamination with air may produce oxidation or yellowing of the product. Bulk storage tanks should also be kept under a dry nitrogen blanket.

Modified MDI, MDI Prepolymers - As with all diisocyanates, modified MDI products will react with moisture. It is imperative that these products also be stored under dry air (dew point less than -40°C/-40°F) or a dry nitrogen pad to prevent contamination. The optimum storage temperatures for the modified MMDI variants vary depending on the product. The recommended storage temperatures for specific modified MDI products are reported in the respective BASF Product Leaflets or Technical Bulletins

Exposure Potential

Exposure of MDI to the general public is highly unlikely due to the low vapor pressure. MDI and products containing MDI are not intended for the general use by the general public.

MDI and products containing MDI are reactive and hazardous chemicals. MDI should only be handled by knowledgeable, well-trained personnel who thoroughly understand the hazards associated with the transportation, storage and use of the chemical.

Workplace exposure should be limited by the use of engineering controls. MDI vapors must be monitored and controlled below applicable regulatory limits. If possible, MDI should be processed within closed systems. When this is impractical, special consideration should be given to ventilation design to limit exposure.

Regulations involving hazardous chemicals are continually evolving and thus exposure guidelines are reviewed regularly and modified whenever new information dictates a change. It is important that all companies handling MDI products are aware of the current legislative requirements.

The guidelines established by OSHA, ACGIH, NIOSH and others, represent current thinking and are believed to be conservative and protective of occupational workers. There is not guarantee of absolute safety.

Risk Management

The potential hazards associated with MDI can be avoided if workers are adequately instructed in supervised on the proper procedures of handling MDI.

Every worker should be trained to realize that exposure to a hazardous chemical requires immediate washing of affected areas using large amounts of soap and water, and that immediate attention may markedly decrease the severity of any health effects. (See First Aid.) Do not wash affected area with solvents.

Protective clothing, gloves, boots and eye protection must be worn whenever there is any possibility of MDI exposure. Protective clothing shall be made of impervious materials. Soiled or contaminated clothing should be laundered or destroyed.

Proper respiratory protective equipment should be readily available and in good working order. Exhaust and ventilating equipment should be inspected and tested regularly to assure MDI vapors/aerosols are being controlled to acceptable levels.

Properly designed emergency showers and eyewash fountains should be placed in convenient locations wherever MDI is used. All employees should know the location and operation of this equipment. All equipment must be frequently inspected to make sure they are in proper working condition.

Federal/Science Findings

U.S. Environmental Protection Agency – Integrated Risk Information System (IRIS)
http://www.epa.gov/iris/subst/0529.htm

U.S Department of Labor – Occupational Safety and Health Administration (OSHA)
http://www.osha.gov/dts/chemicalsampling/data/CH_253300.html

American Conference of Governmental Industrial Hygienists (ACGIH)
http://www.acgih.org

National Institute for Occupational Safety and Health (NIOSH)
http://www.cdc.gov/niosh/topics/isocyanates

Contact Information
http://www.basf.com

MSDS
http://worldaccount.basf.com/wa/PublicMSDS~en_US/Search

Center for the Polyurethanes Industry (CPI)
http://www.polyurethane.org

References

Polyurethane MDI Handbook, BASF Corporation, February 2007