BASF
We create chemistry

MDI Handbook

North America

Table of Contents

1. Emergency Contact Numbers

United States

CHEMTREC ---------- 1-800-424-9300
Human Poison Control Center ---------- 1-800-222-1222
Animal Poison Control Center ---------- 1-800-345-4735
National Response Center ---------- 1-800-424-8802
BASF Emergency Response ---------- 1-800-832-4357

Canada ----------

CANUTEC (Emergencies) ---------- 1-613-996-6666
(Non-Emergencies) ---------- 1-613-992-4624
BASF Emergency Response ---------- 1-800-832-4357

Mexico

SETIQ (Emergencies) ----------01-800-00-214-00
CENACOM (Emergencies) ----------01-800-00-413-00
Polioles Emergency Response ----------011-52-722-265 8600

2. Introduction

Diphenylmethane diisocyanate (MDI) is a member of the diisocyanate family associated with polyurethane chemistry. The term polyurethane applies to a large number of polymers formed through the polyaddition of polyfunctional isocyanates and isocyanate-reactive polyfunctional compounds. Polyurethanes are some of the most versatile polymers in existence today. They exist in numerous forms, ranging from lightweight rigid foams to dense solid compositions, and from soft flexible foams to tough elastomeric moldings.

BASF Commitment to the Polyurethane Industry

The worldwide polyurethane operations of the BASF Group include a broad range of activities such as:

- Urethane chemicals
  - Diphenylmethane diisocyanate (MDI)
  - Toluene diisocyanate (TDI)
  - Polyols (polyether, polyester)
- Polyurethane systems
- Polyurethane elastomers / thermoplastics
- Microcellular polyurethanes

These activities are coordinated on a global basis to assure a high level of quality to polyurethane processors and users throughout the world.

Since its founding in 1865, BASF SE has placed major emphasis on research and development. Today, the results of widely based research activities in Europe and North America are directly available to all independently operating companies in the BASF Group. This constant interchange of technical expertise among businesses in the BASF Group ensures that BASF customers will benefit from the very latest know-how of polyurethane technology within the Group. Figure 1 illustrates the worldwide geographic spread of BASF Group products.

Figure 1. BASF Urethane Chemical Production Sites.

BASF manufactures and markets three of the key urethane chemicals: MDI, TDI, and Polyols. MDI is produced in Geismar, LA, U.S.A.; Antwerp, Belguim; Shanghai and Chongqing, China; and Yeosu, Korea. These facilities produce a full line of MDI products, marketed under the trademark Lupranate® to supply a wide range of polymer applications.

Like many reactive chemicals, MDI products[1] can create hazards if handled carelessly. The purpose of this publication is to outline precautions for the proper handling of diisocyanates under normal and emergency situations. All persons associated with the transportation, storage, or handling of MDI must be thoroughly familiar with the potential hazards and trained in the recommended standard and emergency handling procedures.

This publication is intended only to provide general guidance, and for the area of North America. In some countries, specific regulations supplement or modify the guidance given herein. All users of MDI products must be fully informed on the most current guidelines and regulations of all applicable authorities. Users of MDI are strongly urged to consult the appropriate regulatory authorities before finalizing specifications for processing, handling, and storage equipment. Any technical advice furnished, or recommendation made herein is believed to be reliable but BASF makes no warranty, either expressed or implied, as to its accuracy or completeness or of the results to be obtained.

The current safety data sheet (SDS) should be used in conjunction with this publication because the SDS is updated as changes in regulatory requirements occur. SDSs can be obtained online (http://polyurethanes.basf.us/) or directly from your BASF representative.

[1] In this handbook, the term “MDI products” is often used interchangeably with terms such as “MDI”, “MDI-containing products”, and “MDI materials”.

3. MDI Products

MDI Production Process

In the MDI process, aniline is condensed with formaldehyde to produce methylenedianiline (MDA), and MDA is reacted with phosgene to form MDI. The flexibility of the BASF process makes it possible to control and modify the properties of a broad range of MDI products. This process is designed with the flexibility that allows BASF to be a reliable source of MDI for the polyurethane industry. Figure 2 gives a summary of the MDI, TDI, and polyether polyol production processes.

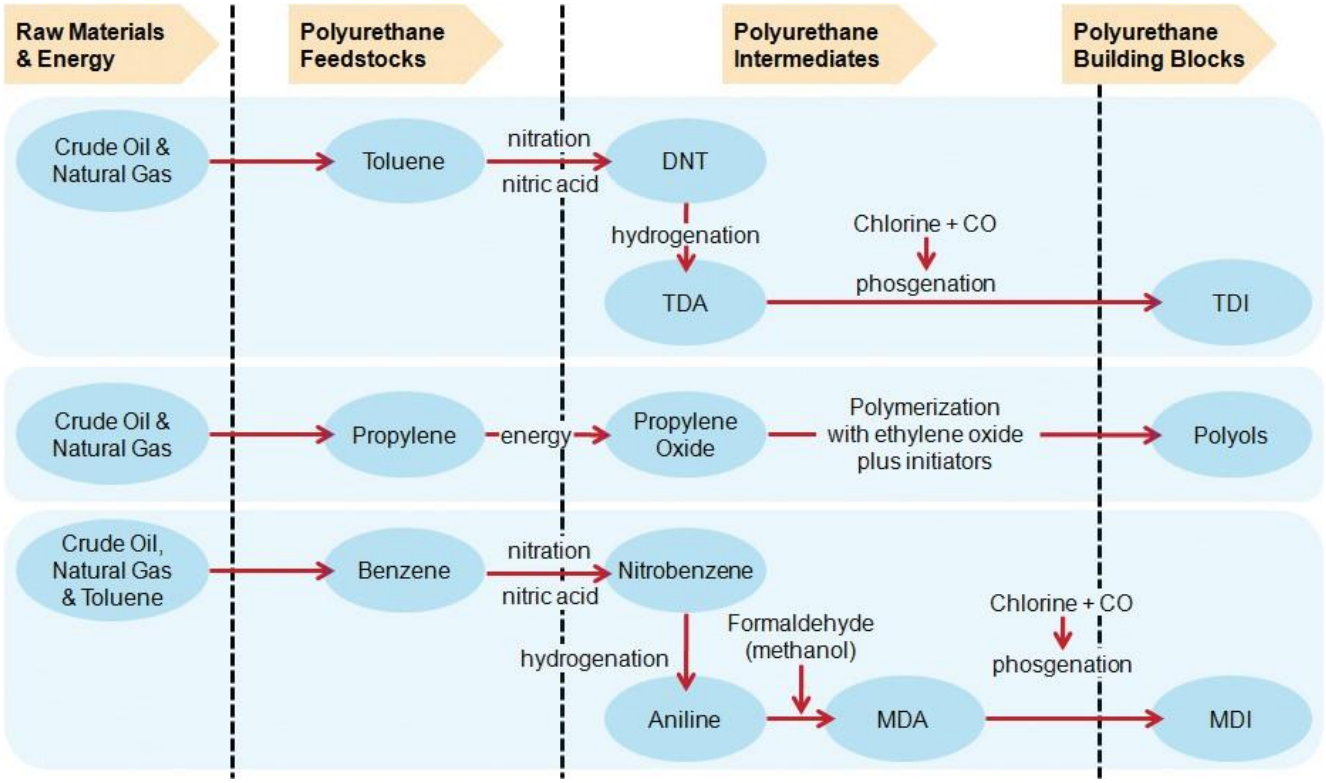
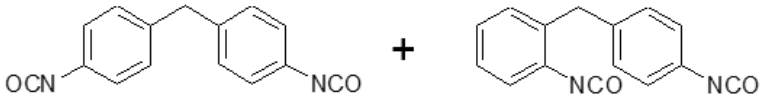


Figure 2. Process summary for the production of polyurethane building blocks.

Figure 3 shows the molecular structure of the primary MDI molecules: Polymeric MDI (PMDI) and Monomeric MDI (MMDI).

Monomeric MDI



Polymeric MDI

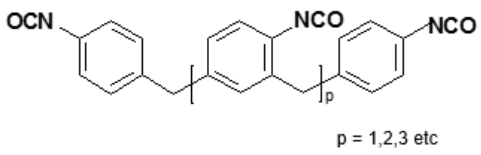


Figure 3. Molecular structure of monomeric and polymeric MDI.

MDI Product Family, Properties, and Applications

MDI is available in three basic types of compositions: PMDI, MMDI, and Modified MDI. MDI and its modified forms are reactive chemicals supplied as liquids or solids. In combination with polyols (polyester or polyether), they are used for the manufacture of cellular (foamed) and non-cellular (compact) polyurethane polymers including textiles, coatings, adhesives, sealants, and elastomers (CASE). BASF MDI Products can be used in many applications within CASE and other markets.

PMDI

PMDI is a brown liquid, stable over a wide range of temperatures. It contains a mixture of polyaromatic isocyanates including 2-ring (MMDI), 3-ring, and higher molecular weight species. As the amount of 3-ring and higher molecular weight species increase, the functionality and viscosity of the PMDI will also increase. PMDI products have a density of approximately 1.23 g/cm^3 at 77ºF (25ºC). PMDI starts to decompose at temperatures above 446°F (230°C) with the evolution of carbon dioxide (CO_2). At 77°F (25°C), it has a low vapor pressure of 10^{-5} mbar ($7.5X10^{-6}$ mm Hg). PMDI is considered to have a low flammability risk due to its high flash point of over 392ºF (200ºC).

The thermal conductivity of PMDI decreases with temperature until approximately 122 to 140ºF (50 to 60ºC), where it increases with temperature (see Table 1). This behavior is somewhat atypical for liquids and is, in part, due to trimerization at elevated temperatures. The dielectric constant of PMDI is 7.3 at 104ºF (40ºC) and 6.5 at 176ºF (80ºC). The conductivity is 1.6 micro-mho at 200 cPs and 1.2 micro-mho at 700 cPs. The coefficient of thermal expansion for PMDI is 0.0008/ºC. Specific heat information for PMDI is listed in Table 2.

Table 1. PMDI thermal conductivity values.

Temperature (°C)	Thermal Conductivity (W cm^{-1} K^{-1})
22	0.00164
48	0.00139
57	0.00155

Table 2. PMDI specific heat values.

Temperature (°C)	Specific Heat (J g^{-1} °C^{-1})
25	1.469± 0.100
50	1.512± 0.100
100	1.577± 0.070
150	1.675± 0.060

PMDI is used in producing high resilience flexible, 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. BASF PMDI products are typically bulk-produced in Geismar, Louisiana.

PMDI Blends and Derivatives

Starting with core PMDI and MMDI products, BASF developed a line of isocyanate blends and derivatives that can deliver the custom properties demanded by specific applications. For example, the 2,4'-MDI enhanced PMDIs are selected for floor coatings that require extra working time, but ultimately maintain cross-linking potential. BASF's PMDI blends and derivatives are available in drums, totes, and bulk quantities.

MMDI

MMDI is a purified material distilled from a PMDI mixture. MMDI refers to the 2,4' and 4,4'-isomers of MDI. Pure 4,4'-MDI is a crystalline solid at room temperature. BASF sells frozen (below 32ºF or 0ºC) drums of 4,4'-MDI as Lupranate® M and MS isocyanates. MMDI is a solid with a melting point of approximately 101.3°F (38.5°C) and a boiling point of 410°F (210°C) at 7 mbar (5 mm Hg). Above 113ºF (45ºC), pure 4,4'-MDI can be shipped and kept as a liquid for up to fourteen days. It starts to decompose at approximately 446°F (230°C). At 77°F (25°C), it has a low vapor pressure of 10^{-5} mbar ($7.5X10^{-6}$ mm Hg). MMDI has a density of 1.20 g/cm^3 and specific heat of 1.39 J/g/ºC at 40ºC (104ºF). MMDI is considered to have a low flammability risk due to its high flash point of 392ºF (200ºC). Increasing amounts of 2,4'-MDI and 3-ring or greater PMDI into the 4,4'-MDI, results in a mixture that is a liquid at room temperature.

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. Our product catalogue displays the several variations in isomer distribution and stabilizer package that are available in the MMDI product line.

Carbodiimide Modified MDI

Given the handling and storage difficulties associated with pure 4,4'-MDI, BASF often uses carbodiimide chemistry to modify and stabilize the MMDI. The carbodiimide-modified isocyanates are liquids that are stable and clear at room temperature. A portion of the MMDI is reacted to yield a carbodiimide-modified isocyanate with a free-NCO weight between 29.2% and 29.5%. The carbodiimide-modification leads to the formation of a trifunctional uretonimine species, by reaction with some of the remaining difunctional MMDI. Therefore, the commercial carbodiimide-modified isocyanates are usually listed as 2.1 functional. Carbodiimide Modified MDI products are used in reaction injection molded (RIM) polyurethane automotive body parts, microcellular elastomers, integral skin foams, flexible foams, adhesives, coatings, sealants, and two-component cast elastomers.

MDI Prepolymers (Quasi-)

BASF offers MDI prepolymers (quasi-) based on the reaction of MMDI, PMDI, and/or carbodiimide modified MDI with a variety of resins, including polyether, polyester, PolyTHF®, and others. A prepolymer results from the reaction of excess MMDI with a hydroxyl terminated resin. The exact term, quasi-prepolymer, refers to a reaction product that is a mixture of prepolymer (capped-resin) and excess MMDI.

Properties of MDI

MDI is denser than water and will therefore sink to the bottom of water-filled containers. Although it reacts with water, the rate of reaction is very slow at temperatures below 122°F (50°C). At higher temperatures or in the presence of catalysts/basic materials, the reaction becomes progressively more vigorous and can become violent. The reaction of MDI with water liberates CO_2 gas and forms insoluble polyurea compounds. These polyurea products often take the form of globules with liquid isocyanate and CO2 trapped inside. These globules can float due to the trapped CO2. The trapped isocyanate will react with water over time.

MDI reacts with acids, alcohols, basic materials (e.g., sodium hydroxide, ammonia, and amines), magnesium and aluminum (and their alloys), metal salts (e.g., tin, iron, aluminum, and zinc chlorides), strong oxidizing agents (e.g., bleach and chlorine), polyols, and water (CPI, July 2003). These reactions may be violent, generating heat, which can result in an increased evolution of isocyanate vapor and/or a buildup of pressure due to CO2 evolution within closed containers.

MDI is not generally corrosive towards metals or other materials at room temperature, but the presence of a small amount of acidity in PMDI can produce some corrosion with copper alloys and aluminum. Copper, zinc, or their alloys must be avoided as they may cause product deterioration. Carbon steel is the recommended material for MDI containers. Stainless steel is the recommended material of construction for pumps, discharge pipelines, and valves. MDI will attack and embrittle many plastic and rubber materials which may cause these materials to crack over time. Flex Hose must be Teflon®-lined or specially sold and labeled for isocyanate handling. Table 3 gives molecular formulas and constants for the three types of MDI. The single MDI forms have been characterized by several identity numbers as made up in this table.

Table 3. MDI molecular formulas and constants.

Species	**Formula**	**Molecular Weight**	**NCO-content (wt %)**
Monomeric MDI	$C_{15}H_{10}N_2O_2$	250.26	33.50%
Prepolymers Modified MDIs	varies	varies	varies
Polymeric MDI	varies	approximately 340	approximately 31%
Reference Numbers			
Chemical Abstracts	2,4'-MDI: 5873-54-1		
	4,4'-MDI: 101-68-8		
	2,2'-MDI: 2536-05-2		
	polymeric MDI: 9016-87-9		
	non-isomer specific: 26447-40-5		
United Nations	4,4'-MDI containing compositions: unregulated		
United States	4,4'-MDI containing compositions greater than 5,000		
	pounds in a single container; NA 3082		
EEC-Number	PMDI: 615-005-01-6		

4. Health Considerations

Acute Hazards
MDI and products containing unreacted MDI are potentially hazardous materials. Therefore, 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 products. Limits have been established for allowable MDI vapor concentrations in the work environment.

MDI can be potentially hazardous in liquid, vapor, mist (aerosol), or dust form. Aerosols are airborne droplets and are present anywhere MDI is sprayed. Aerosols may also be formed when MDI is heated, such as melting pure MDI for certain applications, and allowed to cool in the ambient air. These droplets may present a risk even at room temperature. A dust hazard may arise whenever MDI is absorbed on finely divided materials. If vapors, mists, or dusts are inhaled, MDI can cause respiratory symptoms similar to those caused by other isocyanates.

Some individuals may develop an allergic respiratory reaction (sensitization) to these MDI exposures. Sensitized individuals may thereafter be affected by very low concentrations. After serious vapor overexposure, pulmonary edema can occur. Once sensitized, workers should be excluded from further exposure.

Exposure limits have been established by regulatory agencies and industry groups for MDI. The odor threshold of MDI is approximately 0.2-0.4 ppm; consequently, odor does not provide sufficient warning of overexposure. Table 4 identifies some of the current regulatory limits in effect. Permissible exposure limits (PELs) and ceiling limits should be sufficiently low to prevent sensitization in individuals. However, allergic reactions may occur in sensitized individuals at concentrations well below these values. MDI can produce local irritation upon contact with the skin, upper respiratory tract (nose, throat, and lungs), eyes, and mucous membranes.

Table 4. Regional exposure limits for MDI vapors.

Country	Agencies and Groups	Exposure Limits	ppm	mg/m^3	Notes
Canada					
Alberta		TLV	0.005	0.051	8 hrs TWA
British Columbia		TLV	0.005	0.051	8 hrs TWA
		PEL	0.01	0.1	Ceiling Limit
Ontario		TLV	0.005	0.051	8 hrs TWA
Québec		TLV	0.005	0.051	8 hrs TWA
U.S.A.	ACGIH	TLV	0.005	0.05	8 hrs TWA
	OSHA	PEL	0.02	0.2	Ceiling Limit

These values are subject to change and are given here only as examples of present limits.
ACGIH - American Conference of Governmental Industrial Hygienists
PEL - Permissible Exposure Limit
Ceiling Limit - Concentration that should not be exceeded
STEL - Short Term Exposure Limit (15 min exposure)
TWA - Time Weighted Average
TLV-Threshold Limit Value
OEL- Occupational Exposure Limit
WEL - Workplace Exposure Limit
OSHA - Occupational Safety and Health Administration

Effects on the Respiratory System
Concentrations above the occupational exposure limit (OEL) 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.

The inhalation LC_{50} (aerosol-4 hours rat) has been determined to be approximately 180 mg/m^3 (MMDI) and 490 mg/m^3 (PMDI). The MDI vapor concentration in a saturated atmosphere (13 ppb) is approximately 4,000 times lower than the LC_{50}. No mortality in rats was observed at this concentration.

Effects on Eyes
Direct eye contact with MDI products may produce watering, irritation, and inflammation of mucous membranes. Discharge may result.

Effects on Skin
Skin contact with MDI may result in irritation and a mild tanning reaction, 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. Prolonged contact can cause reddening, swelling, rash, scaling, or blistering.

Effects on Ingestion
The effects of ingestion include irritation of the mouth, esophagus, and stomach. The harm that occurs will be a result of this irritation and not any system toxicity. The LD_{50} (oral- rat) for MDI is greater than 2,000 mg/kg.

Chronic Hazards
Repeated overexposure of the skin, the eyes, nose, or upper respiratory tract may cause chronic irritation. Some individuals may develop a hypersensitivity to MDI vapors and, upon exposure to minute amounts of this material, experience difficulty in breathing. Long-term overexposure to diisocyanates has also been reported to cause lung damage, including reduced lung function, which may be permanent.

Sensitization
Sensitization is an effect whereby a physiological response (e.g., respiratory or dermal) is caused by re-exposure to a low concentration of chemical in an individual following higher, initial acute exposure, or chronic exposures. The response may be immediate, delayed, or both.

The symptoms associated with respiratory sensitization by diisocyanates are similar to those of asthma. These include difficulty in breathing, chest tightness, wheezing, and coughing. If sensitized individuals continue to work with MDI, the latency period between exposure and the onset of symptoms may be shortened, and the severity of the symptoms may increase. Upon removal from MDI exposure, the sensitized individuals' respiratory problems usually improve. If a sensitized person continues to be exposed, his/her respiratory problems can become permanent. Therefore, early recognition of sensitization by a physician specialized in lung diseases and prevention of subsequent exposure is important to protect the respiratory health of sensitized workers. It is believed that cross-sensitization may occur between different isocyanates. Meaning individuals sensitized to other isocyanates may also demonstrate sensitization to MDI. Responses in sensitized individuals vary considerably from one individual to another.

The 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, especially in sensitized individuals. If anyone experiences an exposure severe enough to develop symptoms, no matter how mild those symptoms may appear, a physician should be consulted prior to resumption of work with MDI.

First Aid

<u>First Aid in Case of Inhalation</u>
Affected persons should exit the contaminated area to fresh air supply immediately. Remove all contaminated clothing and contact medical personnel immediately.

Keep affected persons comfortable and warm. Medication will rarely be necessary if adequate fresh air is immediately available.

If there has been a severe exposure and breathing stops, artificial respiration should be initiated immediately. If oxygen inhalation equipment is available, oxygen should be administered by a physician or authorized person.

Never attempt to give anything by mouth to an unconscious person. Medication should be given only under the direction of an attending physician. In the event of breathing difficulty, a physician or authorized person should treat with medication[2] to help prevent over-reaction of the immune system and pulmonary edema.

In cases of exposure to mists or liquid MDI, immediate decontamination is essential. First responders must wear respiratory protection and avoid direct skin contact with contaminated surfaces, skin, and clothing.

First Aid in Case of Eye Contact
In the event MDI contacts the eyes, immediately flush affected area with running water for at least fifteen minutes. The eyelids should be held apart during washing to ensure contact of water or propylene glycol for skin cleaning with all affected tissues of the eyes. The affected person should receive medical attention, preferably from an eye specialist, as soon as possible.

First Aid in Case of Skin Contact
Immediately move the affected person to a safety shower or other source of large amounts of water. Remove all contaminated clothing while under the shower and thoroughly wash affected areas with soap and water for at least fifteen minutes. Medical treatment should be given if skin irritation persists (e.g., redness, swelling, or burning sensation). Launder contaminated clothing in decontaminating solution and launder before reusing or destroy in cases of severe contamination. In all cases, always take precaution against additional exposure from contaminated surfaces and materials when completing these activities.

First Aid in Case of Ingestion
If MDI is ingested, immediately contact the Human Poison Control Center (1-800-222-1222). The affected person should immediately drink large amounts of water to reduce the concentration of the chemical. Vomiting should not be induced. Keep the individual calm and protect against loss of body heat. The person should be transported to a medical facility as quickly as possible. If vomiting should occur, more water should be given immediately. Never administer anything by mouth if the person is unconscious or having convulsions. Immediate medical attention should be provided.

Medical Considerations
Preplacement medical surveillance including pulmonary function testing should be given to individuals being assigned to work with MDI. All personnel should receive a thorough health appraisal, including examination of the upper respiratory tract and lungs.[3]

Individuals with the following conditions should receive special consideration by a physician prior to placement in positions where diisocyanates may be contacted:

- Chronic diseases of the nose, throat, or lungs.
- History or presence of asthma or asthmatic bronchitis.
- Recurrent eczema or pulmonary sensitization.

The incidence of illness due to working with MDI will be minimized if appropriate industrial hygiene measures are consistently enforced. The duration of sensitization is not known. General practice is to consider sensitization permanent. Therefore, any sensitized individual affected by exposure to minuscule amounts of MDI should be assigned to work in an isocyanate-free environment.

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

[2] E.g., Dexamethason inhaler (Dexamethason-21-isonicotinate).
[3] Tests may include but are not limited to pulmonary function or spirogram with emphasis on Forced Vital Capacity (FVC) and Forced Respiratory Volume (FEV 1-sec).

Every worker should be trained to realize that exposure to a potentially 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). Never wash affected areas with solvents, as this could increase the absorption of MDI through the skin.

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. Additional information is available at:
https://polyurethane.americanchemistry.com/Products-Resources-and-Document-Library/
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.

5. Safe Handling of MDI Products

MDI and products containing MDI are reactive and potentially hazardous chemicals. MDI should only be handled by knowledgeable and well-trained personnel who thoroughly understand the hazards associated with the transportation, storage, and use of the chemical. Eating, drinking, and the use of tobacco products should not be allowed where MDI is handled or stored. Contaminated clothing must be washed before reuse or discarded if severely contaminated. Never reuse contaminated footwear or leather gloves.

Employee Training and Education
The investment in employee education and training on proper storage and handling procedures for MDI is extremely important. Hazardous situations may be created by poorly trained personnel, even in well-designed operations. All personnel that may come into contact with MDI products should be included in a hazard communication training program. Employee training and education programs must include the regulations of all applicable agencies. Local regulations and requirements can be obtained from the local authorities. Additional information is available at:
https://polyurethane.americanchemistry.com/Products-Resources-and-Document-Library/

Operating procedures, including all safety rules should be reviewed by all personnel regularly. Safety procedures and rules should be posted in work areas accessible to all individuals. Safety equipment should be available and maintained in good working order.

Engineering Considerations
Building design considerations can reduce the potential hazards associated with the storage and handling of MDI. Careful consideration should be given to the design of the building's ventilation system. MDI aerosols or vapors must be monitored and controlled below applicable regulatory limits. If possible, MDI should be processed within closed systems. There are some applications where this is impractical, however, such as laminate board and composite wood production, spray systems, or laboratory areas. Special consideration should be given to ventilation design and respiratory protection in these applications.

The guidelines established by the Occupational Safety and Health Administration (OSHA), American Conference of Governmental Industrial Hygienists (ACGIH), National Institute for Occupational Safety and Health (NIOSH), and others represent current thinking and are believed to be conservative and protective of occupational workers. Regulations involving hazardous chemicals are continually evolving and thus exposure guidelines are reviewed regularly and modified whenever new information dictates change. It is important that all companies handling MDI products are aware of the current legislative requirements in each jurisdiction.

Additional Precautions
Care should be taken to prevent contact of water with MDI. Water reacts readily with MDI and is the most common contaminant of diisocyanates. The hazard associated with this reaction is the formation of CO_2 and the resultant increase of pressure in closed containers. Even small quantities of water can cause significant problems and the following safety recommendations must be observed:

- Store MDI in a dry environment using dry air or nitrogen pad[4].
- Plug and cap all lines leading to and from storage tanks.
- Fittings and line connections should be maintained and stored in a dry environment.
- Do not tightly close any container of MDI that has been, or is suspected of having been, contaminated with water.

Contamination by basic compounds such as caustic soda, amines, or other similar materials must be avoided. The reaction of MDI with these materials may cause the generation of heat and CO_2. The liberation of CO_2 in tightly closed or restricted vessels or transfer lines may result in violent rupture.

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

Personal Protective Equipment
Personal protective equipment (PPE) is not an adequate substitute for safe working conditions. However, in many instances including emergency situations, it may be the only means of protecting the worker. Only individuals wearing this equipment are protected. Unprotected personnel should be removed from any work area where there is the potential for exposure to MDI.

Eye Protection
Chemical safety goggles are required for all persons handling MDI, especially where there is the possibility of splashing, spraying, or MDI-coated dust. Cup-type or rubber-framed goggles equipped with the approved impact resistant glass or plastic lens are recommended.

Respiratory Protection
MDI vapor concentrations exceeding PELs may occur. Such occasions include (but are not limited to) the following:

- Spray operations
- Opening of tank car hatches, truck man-way covers, or drums that have been heated
- Connecting or disconnecting of hoses and pipes
- Equipment operation or repair
- The breaking or failure of MDI piping or equipment
- Any spill or leak of MDI that is heated

Personnel must not enter an area where MDI vapor concentrations or aerosols may exceed the recommended exposure limits without appropriate PPE. Personnel who may be exposed to spills and anyone involved in generating MDI aerosols, as in spraying operations, or in the high temperature processing of MDI products, must be provided with adequate respiratory protection.

Respirators must be approved by applicable authorities and a written respiratory protection program with medical surveillance must be implemented. In the United States, an air-purifying respirator (APR) can be used provided that (1) the respirator is equipped with an end-of-service life indicator (ESLI) certified by NIOSH for the contaminant (there is no ESLI for MDI), or (2) if there is no ESLI appropriate for conditions in the workplace, the employer implements a change schedule for canisters or cartridges that is based on objective data that will ensure that canisters and cartridges are changed before the end of their service life. Therefore, an employer must select a cartridge or canister recommended by the manufacturer and must then implement an appropriate change-out schedule. The data relied upon and the information forming the basis of the determination must be included in the employer's written respiratory program.

If APRs cannot provide appropriate protection, respiratory equipment must be an air-supplied (SAR) or self-contained breathing apparatus (SCBA) with full-face piece operating in pressure-demand or other positive pressure mode.

Respiratory protection equipment must be carefully maintained, inspected, and cleaned regularly. Equipment should be easily accessible, and personnel should be thoroughly trained on the proper selection, maintenance, and use of equipment.

Head, Skin, Hand, and Foot Protection
Head protection should be worn to protect from falling objects, overhead leaks, and splashes. A long sleeved, impervious protective suit should be worn whenever there is possibility of exposure to MDI. Impervious gloves[5] should be worn whenever the possibility of spills or splashes exists.

Personnel handling MDI drums and cans should wear protective safety shoes with built-in steel toecaps. Rubber overshoes may be worn with ordinary work boots. Never wear uncovered leather shoes. Leather will absorb MDI, making decontamination of leather products such as gloves or shoes difficult.

[5] See the Center for the Polyurethanes Industry (CPI) website (http://www.polyurethane.org) for recommendations on glove permeation data.

Surfaces should be thoroughly washed with soap and water after mild contamination.

Fire Hazards

Due to its high flash point (392ºF or 200ºC), liquid MDI does not constitute a severe fire hazard. However, it is important that the proper fire-fighting equipment be available in case it should be needed.

Water spray is effective for extinguishing fires covering large areas. Automatic sprinkler systems may be helpful in certain applications. When water is used to extinguish MDI fires, it should be applied in large amounts. Small amounts may only react with the hot MDI and worsen the fire situation. CO_2, protein foam, or dry chemical extinguishers are also effective.

Do not inhale gases or fumes from burning MDI, as they can contain carbon monoxide, nitrogen oxides, MDI, and small amounts of hydrogen cyanide.

Fire fighters should wear self-contained breathing apparatus. Appropriate personal protective equipment (PPE) should be worn including turnout coat, boots, gloves, and helmet.

6. Shipment of MDI

Although MDI is a hazardous material in terms of reactivity and toxicity, it can be transported and handled safely provided that appropriate precautions are observed.[6]

Regulations
The shipment of MDI and MDI-containing products are subject to strict regulations within most countries in Europe and North America when exceeding 5,000 pounds of 4,4'-MDI in a single container. In addition, the international movement of these products by road, rail, or sea is subject to international agreements which provide specific requirements concerning shipment which must be observed by all parties involved.

The transportation equipment for MDI products must meet the design and construction requirements of national and international regulations. Table 5 is a partial list of transportation regulations.

Table 5. Transportation regulations.

Regulation	Description
DOT	United States Department of Transportation Rules Governing the Transport of Hazardous Materials (HMR)
ICAO	International Civil Aviation Organization
IMDG	International Maritime Dangerous Goods Code
IMO	International Maritime Organization
TDG	Canadian Regulations Concerning the Transport of Dangerous Goods by Land

BASF uses only professional transportation companies whose personnel are competent and well trained in handling of MDI products. Accompanying all shipments of MDI products is an emergency response guide and/or a Bill of Lading.[6]

Shipping Containers
MDI products are generally shipped in 500 - 550 pound steel drums or in bulk. Bulk deliveries are generally made in tank trucks (road tankers) and demountable tanks containing approximately 20 metric tons (approximately 44,000 pounds) or tank cars (rail tank wagons) containing up to approximately 86 metric tons (approximately 190,000 pounds). Each container should clearly display a tag, placard, and/or label warning of potential hazards.

The MDI product quality can be affected by temperature. The recommended temperature must be maintained throughout transit to maintain product quality. Refer to the specific product information for the temperature requirements of individual products in the BASF Product Leaflets or Technical Bulletins.

For further information concerning distribution refer to:[6]

a) Technical Data Sheets of MDI products Lupranate®.
b) See References: *Guidelines for the Safe Loading, Transport & Unloading of MDI & TDI in Bulk* (ISOPA, February 2006). *MDI Transportation Guidelines* (CPI, 2002).
c) Specific regulations for Europe, America/U.S.A., and Asia.

MDI containers must remain closed until use in order to prevent moisture contamination. Only trained individuals wearing appropriate PPE are allowed to open containers of MDI products. When an MDI container is opened, make-up dry air or nitrogen should be provided.

BASF has the responsibility to ensure that all MDI shipments leaving BASF facilities are properly prepared to comply with all the appropriate regulatory transportation requirements. Depending on the method of transportation, the rail carriers, truck lines, or airlines are responsible for the safe shipment of MDI products from the shipping

[6] CPI has published recommendations for the transport of MDI in the United States. See Reference: *Guidelines for Receiving and Unloading MDI (AX-198, 2014)*.

point to the final destination. Emergency situations, such as accidents or leaking containers, must be reported immediately to appropriate regulatory authorities and to BASF (see Section 8).

Unloading Operations
The operation of unloading (or loading) any tank truck, iso tank container, tank car, or small container of MDI is potentially hazardous operation. Unloading facilities must be designed and located giving due regard to the potential hazards of MDI products.

Written operating procedures covering all aspects of the unloading operation of MDI products must be prepared and available to all involved parties. All necessary PPE and emergency equipment must be available for the unloading operations. Personnel must be trained in the procedures and correct use of all protective clothing and emergency equipment (see Section 5).

Bulk Unloading
Unloading of MDI products from bulk containers should be performed with a self-priming, seal-less pump and a vapor return line connected between the storage tank and the bulk delivery container. The seal-less design eliminates potential seal failure. Due to the MMDI freezing point, MMDI transfer lines must be heated. Dry air or nitrogen must be available to purge the unloading lines and vapor return line after unloading is completed. The storage tank must be equipped with a high-level device which will stop the unloading automatically if the maximum tank level is reached.

If dry air or nitrogen pressure is used to transfer MDI products from a bulk container to the storage tank, the pressure must be regulated below the maximum safe operating pressure of the bulk container. The storage tank vent must be sized accordingly. After disconnecting hoses, all exposed fittings and hoses must be protected with caps or plugs.

The dimensions and physical arrangement of bulk containers vary. Contact your local BASF representative for unloading (and loading) instructions on specific container types. Procedures are available for MC-307 tank trucks and 20,000-gallon rail cars.

Drum Handling
The handling of MDI drums is a potentially hazardous operation. Operators must use the proper PPE during handling. Transportation of drums should be completed by lifting to avoid damage caused by sliding or rolling. Only equipment designed for drum handling should be used. Drums should be handled and unloaded carefully to prevent damage. Improperly equipped fork trucks may result in punctured or damaged drums. Forklift trucks equipped with "parrot beaks" or drum clamps are ideal. Each shipment should be closely examined for damaged or leaking drums. If leaking drums are found or damage occurs during movement, refer to Section 8 for procedures on proper handling of leaks or spills.

Liquid MDI products which have solidified through cooling should be liquefied by careful heating as soon as possible. For correct heating methods and temperatures, see the appropriate Technical Data Sheet.

Drums can be emptied using a standard immersion pump or gravity discharged. Air displaced from the receiving tank should be discharged to the vapor exhaust system. A silica gel filter should be connected to the open drum vent (small bung) to prevent drums from collapsing while being emptied. The filter will also prevent moisture contamination from occurring. The opening of MDI drums should be minimized to reduce the risk of moisture contamination.

Water contamination of drums must be avoided. Contamination with water can result in pressure build-up in closed containers by the generation of CO_2 gas from the water-MDI reaction. Drums showing evidence of pressure buildup must be vented immediately. If the drum is not vented, violent rupture may result.

Refer to Section 7 for storage of MDI drums and Section 9 for recommendations on the neutralization and disposal of empty MDI drums.

Sample Shipments

In order to ensure that small packages are safe for transport, customers should contact BASF for information concerning the regulations and restrictions that apply. This is especially true when the customer does not normally ship small samples of hazardous materials and may not have the proper packaging material. BASF will not accept unsolicited samples of MDI products.

7. Storage

Storage and Handling Considerations
A thorough knowledge of the chemical and physical properties of MDI, as well as all federal and local regulations and building codes, is necessary for the safe handling and storage of MDI products.

When designing storage systems for MDI, extreme care must be exercised to avoid contamination with water, strong bases, or other active hydrogen-containing compounds. Acids, bases, and other polyurethane catalysts should not be stored in the same area as MDI.

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 392°F or 200°C), it 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.

PMDI
To maintain product quality, it is important that PMDI products be stored and handled correctly. It is imperative that PMDI products be stored under dry conditions. Storage tanks should be maintained under positive pressure pads with dry air or nitrogen.

The storage temperature will affect the handling characteristics and product quality of PMDI. The most favorable temperature for storage is 68 to 86°F (20 to 30°C). The recommended storage temperatures for specific PMDIs from BASF are reported in the respective BASF Product Leaflets or Technical Bulletins.

The viscosity of PMDI is temperature-dependent. At temperatures below those recommended, PMDI may be difficult to pump or pour. Raising storage temperatures to the recommended levels will return PMDI viscosities to their typical levels. At extremely low temperatures, it is possible for some of the material to crystallize. The crystals can be melted by heating the material in a hot air oven to 140 to 158°F (60 to 70°C) maximum. Once the material has melted, return the product to the recommended storage temperatures.

PMDI should not be held at 158ºF (70°C) for more than four hours or the product will begin to degrade. If the product is stored above the indicated temperature range, degradation may also occur. Degradation is indicated by slow, irreversible buildup in viscosity. If these directions are followed, a storage life of to nine months can be expected for PMDI products, with specifics by products in BASF Product Leaflets or Technical Data Sheets.

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., <32°F or <0°C). Below this temperature, the rate of dimer formation is minimized. If it is kept under dry nitrogen the product may be stored up to six months after the 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 176 to 212°F (80 to 100°C). The drum contents should not be heated above 158°F (70°C) 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 not recommended because of the potential danger of drum leakage.

When MMDI is to be stored or processed as a liquid, the optimum temperature for storage is between 104 and 111°F (40 and 44°C). Liquid MMDI when stored with a dry nitrogen blanket will retain its properties for up to fifteen

days, though dimer content increases significantly beyond five days. If the product is kept outside this range, it will degrade quickly. Figure 4 shows the rate of dimer formation as a function of storage temperature for MMDI. The rate of dimer formation is greatest just below the melting point (100°F or 38°C) for the solid, and above 122°F (50°C) for the liquid. Liquid MMDI must be stored under dry nitrogen because contamination with air may produce oxidation or yellowing of the product.

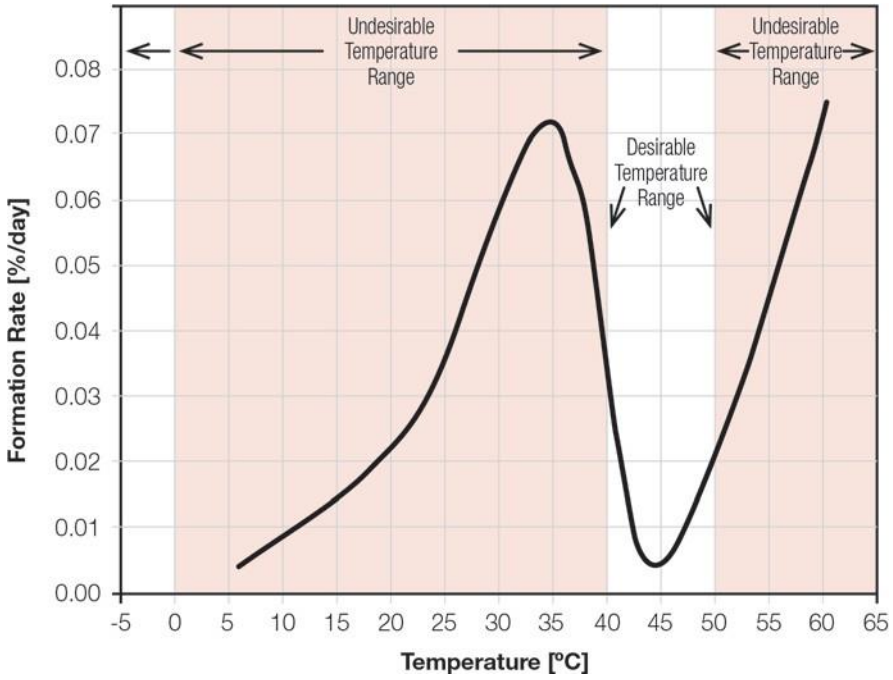


Figure 4. Lupranate® M: Rate of dimer formation as a function of storage temperature.

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 or nitrogen pad to prevent contamination. The optimum storage temperatures for modified MDI vary depending on the product. The recommended storage temperatures for specific modified MDI products are reported in the respective BASF Product Leaflets or Technical Data Sheets.

If the material is stored below the suggested temperature range, it may begin to crystallize. The crystallized material contains a high concentration of MMDI and will exhibit similar dimerization characteristics. Action must be taken quickly to solubilize the material by heating the product to 140°F (60°C). To minimize additional dimer formation, the drum contents should not be heated above 158°F (70°C). If these materials are stored above the recommended temperatures, the product will begin to degrade. This degradation is indicated by a slow increase in viscosity, slight turbidity, and sediment formation. If these products are stored in the recommended temperature range and moisture is excluded, a shelf life of at least six months can be expected for most products.

Storage Tank Design

All MDI storage tanks must be blanketed with dry air or nitrogen. MMDI must be stored under dry nitrogen because contamination with air may produce oxidation or yellowing of the product. Storage tanks should be maintained under slight positive pressure (1 mbar). Storage tanks should be pressure-controlled, preferably by nitrogen or dried air. Storage tank ventilation can be accomplished by pressure control through an activated carbon filter or knockout pots. The ventilation lines and the carbon filters must be maintained frequently for proper function. In all instances, MDI venting procedures must comply with applicable codes, regulations, and permits. In the United States, OSHA requires hazard communication labels for all containers of MDI products.

Each MDI product has its own prescribed storage temperature. The customer must maintain the storage temperatures as recommended for individual products.

To maintain the desired product temperature, MDI storage tanks should be equipped with a temperature indicator, heat tracing, and insulation. Indoor storage tanks are recommended for MDI applications, but outdoor storage tanks may be used. If using an outdoor storage tank to store MDI, the tank should be insulated, have a heating source if necessary (e.g., heating jacket, heating coils, or heat exchanger), and a top mounted agitator to avoid local overheating if necessary. All MDI storage tanks should be located above ground and be certified for positive pressure for unloading or if contamination occurs.

The preferred method of temperature control is external heat exchangers using an inert heating medium. External tempered water and electric tracing have been successfully used. Steam should not be used due to the possibility of overheating. Any moisture contamination must be prevented. To eliminate any potential of a coil leak, internal coils are not recommended. Heating coils and heat exchangers should be checked for corrosion regularly.

MDI tanks should be equipped with level indicators and separate high-level alarms and cutoffs to prevent accidental overflow. Tank areas must be diked to prevent runoff in the event of an MDI release. Diking must be sufficient to contain potential spills and leaks and prevent accidental release of MDI to sewers, waterways, or public thoroughfares. Dikes must be designed for 1-1/2 times the tank capacity or as directed by codes and regulations for handling hazardous chemicals. Storage tanks should be able to hold entire MDI shipments (i.e., if the shipment is typically by rail car, the storage tank should be greater than the capacity of the rail car).

Tanks may be fabricated of unlined carbon steel. The steel tanks should be rust-free because trace iron contamination may affect the MDI reactivity. Other satisfactory materials include stainless steel, glass-lined steel, or nickel-clad steel; however, these configurations are more expensive. For additional information, please refer to CPI guidance document AX-365 (United States).

Drum Storage

Drum storage areas should be covered and well ventilated. Ideally, MDI drum storage areas should be diked and separated from materials reactive with MDI. All storage areas should be arranged in an orderly manner, leaving doorways or exit routes clear. Local codes may have specific requirements for the storage of hazardous chemicals. Many local authorities reference the International Fire Code when making decisions on MDI drum storage. Information on the International Fire Code may be obtained at the following website: https://codes.iccsafe.org/content/IFC2015/toc

Intermediate Bulk Containers (IBCs), or totes, may be of interest because they may reduce the problem of drum disposal.[7] Contact your local BASF office to determine the availability of IBCs.

[7] IBCs are not recommended for shipment of MMDI due to its relatively high freezing point (100ºF or 38°C).

8. Emergency Procedures

Guidelines for Dealing with MDI Product Incidents[8]
All incidents are unique so it is not possible to write guidelines to deal with every circumstance. Each incident must be assessed from the information available.

All people involved with the handling or transportation of MDI must be aware of the hazards associated with MDI, the appropriate emergency procedures, and their individual responsibilities in the event of any emergency involving MDI.

The primary response to any release of MDI, whether a transportation incident or an in-plant spill, is to evacuate all unprotected people to a safe location. Only then should properly trained and protected personnel (see Section 5) evaluate, contain, stop, clean up, and decontaminate any spill. The odor threshold of MDI is above the established exposure limits for MDI. Areas should not be considered free of diisocyanate vapors until the area has been monitored.

Depending upon the size, location, and type of release, government agencies or authorities may require notification. In the United States, transportation incidents of over 5,000 lbs. to the environment must be reported to the National Response Center (NRC) (1-800-424-8802) and the local planning commission as outlined under Emergency Planning and Community Right-to-Know Act (EPCRA) regulations. Transportation incidents involving MDI must be reported to the NRC for any release over the reportable quantity of 5,000 lbs. (approximately 500 gallons). This is a requirement of United States Federal Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regulations. Regulations involving the release of hazardous chemicals are continually evolving, therefore, it is important that all companies handling MDI be aware of the current legislative requirements in each jurisdiction.

Each plant should have a system for dealing with emergencies within the plant. Such systems are only effective if regularly practiced. It is appropriate to form a plant fire crew and emergency team so a well-trained team can quickly address an emergency. Everyone, however, should be aware of the hazards involved and the limitations of self-help. The top priority should always be to save a life rather than limit physical damage.

Spill and Leaks
Only properly trained and equipped personnel (see section 5) should attempt to clean up spills and leaks. The spill should be contained, and the leak stopped to prevent further contamination. It is necessary to distinguish between minor incidents, such as those that may occur in a laboratory or a workshop handling MDI regularly, and major spills, such as a bulk tank truck release. The most important criteria for distinguishing between the two is the ability of present personnel to deal with the occurrence, rather than the actual size of the release.

<u>Minor Incidents</u>
For small spills or leaks, trained people wearing appropriate PPE and respiratory protection should ventilate the area by opening doors and windows, then completely cover the spill with an absorbent material such as an all-purpose oil absorbent, dry sand, or cat litter.

Use more than enough absorbent material to absorb all of the liquid MDI. Shovel or scoop the absorbent into an open top container and move to a safe location for neutralization. Do not tightly seal this container since the MDI will react with any moisture present and generate CO_2 gas, which could cause a sealed container to burst.

Decontaminating or neutralizing solutions are mixtures of agents that react with the MDI and agents that promote the reaction. The choice of solution will depend on the location (inside or outside), temperature (below or above freezing), and the flammability requirement for the intended use. A typical decontaminating solution can be made by mixing water (90-95 vol%), household ammonia (3-8 vol%), and liquid detergent (1-7 vol%). The water and ammonia will react with the MDI to form polyurea solids and CO_2 gas, and the detergent helps promote the

[8] For emergency procedures at incidents for bulk vehicles, drums, and IBCs see Reference: *MDI Transportation Guidelines* (CPI) (Only for the United States).

reaction. Soda ash (Na_2CO_3) may be used instead of ammonia resulting in a less active decontamination solution. This solution works well indoors at room temperature. It is important to note the hazards and regulatory limitations of any neutralizing solution.

After the drums containing the shoveled sorbent material are moved to a safe area, apply neutralizing solution and allow it to stand with a loose-fitting cover at least 48 hours. The container may be sealed after 48 hours. The container should remain vented (loosely covered) to prevent any pressure buildup, and the contents of the container properly disposed (see Section 9).

After the absorbent has been removed from the spill site, the site should be washed and scrubbed with neutralizing solution. Allow the solution to react for at least ten minutes. Once the area is cleaned it should be tested for diisocyanate vapors. If MDI vapors continue to be present, the decontamination should be repeated until the area is free of MDI vapors.

Solid neutralizers, which are neutralizers premixed with an absorbent, may be used for the quick clean-up of very small spills.

Ammonia may be regulated as a hazardous material. Before using ammonia, refer to any exposure limits and applicable regulations. The use of sawdust in combination with any decontaminate solution may cause auto-ignition.

Large Spills

For large spills of MDI, immediate emergency response is necessary to contain the release. This may require notification of local emergency response services such as the fire department. Such an event should be factored into every MDI user's community awareness program.

All persons should be evacuated to a safe location. Properly trained and equipped personnel should then isolate and contain the spill. MDI should be contained and not be allowed to flow into any sewers or waterways.

Once the spill has been isolated and contained, the appropriate clean-up procedures should be used to remove and decontaminate the MDI. Transfer as much liquid as possible via pump or vacuum device into closed but unsealed containers for disposal. Absorbent material and decontaminating solution should then be used as described in the previous section regarding minor spills to clean the area. For specific instructions or assistance, the BASF emergency help line is available 24 hours a day in the United States (1-800-832-HELP).

For transportation incidents in the United States, the American Chemistry Council (ACC) operates CHEMTREC. The CHEMTREC number (1-800-424-9300) is available 24 hours a day and is on all BASF Bills of Lading and SDSs. A call to CHEMTREC will set the emergency response notification process in motion as well as provide emergency response information to response personnel. A list of emergency response contact numbers for the United States, Canada and Mexico can be found in Section 1 of this handbook.

MDI Involved in Fires

All involved personnel must put on self-contained breathing apparatus and complete chemical protection (i.e., rubber gloves, boots, goggles, and protective clothing). All nonessential personnel must evacuate the immediate area. The fire should be extinguished using one of the following:

a) Dry chemical powder
b) Protein-based foam
c) CO_2 extinguisher
d) Large quantities of water

Once the fire is extinguished, the next step is to prevent spilled material from spreading by using collection containers and absorbers such as sand or earth.

The use of water or foam to extinguish the fire and cool the container makes it likely that moisture will enter the damaged tank or drum. Since water reacts with MDI to form solid polyureas and CO_2, the danger exists of the

damaged area becoming plugged, resulting in pressure buildup. To prevent damage to the tank, it must be vented.

Depending on the condition of the tank and/or vehicle, the MDI product should be transferred to another container for disposal. This new tank must also be vented. In any case, the MDI product should not be shipped until the degree of water contamination is clarified.

If the MDI product is stored in the vicinity of a fire but not directly involved in the fire, the container should be moved clear of the area. If the container or tank cannot be moved away from the fire, a water curtain should be positioned between it and the fire. If this cannot be accomplished safely, the tank should be cooled using a direct water spray. This should prevent damage to the tank body and its contents.

Pressurized Drums
A bulging drum of MDI should be assumed to be the result of contamination of the product, usually with water. This slow but unstoppable reaction with a diisocyanate produces CO_2, which increases the pressure inside the container. Since it is not easy to judge the acute risk of bursting, the drum under pressure should not be moved. A tarpaulin tarp should be placed over the drum.

It is necessary to relieve the pressure safely before the drum bursts. This is best accomplished by puncturing the top of the drum with a long-handled spike. Some response companies have specialized drum puncturing devices. During this action, all uninvolved persons must be removed from the area and the working personnel must have complete chemical protection.

The punctured drum must then be placed in an oversized drum with pressure venting capabilities. Remember that the original contamination will probably continue to cause a pressure increase, so the container must be regularly vented using proper precautions. Contact BASF for disposal recommendations.

Chemical Reactions
The combination of polyol and diisocyanate components yields large amounts of heat and gas evolution. An evacuation of the immediate surroundings should be considered because of the potential large amounts of heated MDI vapors that can be evolved. All personnel involved must wear complete protective equipment. The reaction, once begun, cannot be stopped and the goal must be to prevent pressure buildup by venting. In most instances, controlled venting via the safety valve may not be possible due to the safety valve becoming plugged with foam or solids. If possible, stop uncontaminated material from entering the reaction by pumping it into a separate vessel.

Although difficult with insulated tanks, cooling should be attempted. Any vapors should be knocked down with water spray or foam. The reaction should proceed to end with a minimum of heat and vapor evolution.

9. Environmental Considerations

The following recommendations should be interpreted in light of existing and future legislation. The disposal of liquid MDI wastes and used containers may be regulated by local, state, provincial, and federal agencies.

Disposal of Waste MDI Products
MDI products are classified as non-hazardous materials for disposal per US Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) and Canadian Provincial regulations. There are three basic methods for disposing of liquid MDI wastes. The choice of method will depend in part on the amount of waste to be treated and the availability of decontaminants. It is important to note that some states have greater restrictions than federal regulations and may consider MDI to be a hazardous waste. Be sure, therefore, to check with the appropriate state and regulatory agencies before disposing of waste MDI or MDI-based polyurethane foams.

Method 1: Incineration
Incineration under approved, controlled conditions is the preferred method for all but small amounts of MDI product. It should, however, only be done in properly monitored equipment specifically designed for the disposal of noxious chemical wastes and properly permitted by the local, state, provincial, and federal agencies. In the United States, only federally approved incinerators may be used.

Method 2: Reaction with Liquid Decontaminants
The waste MDI product should be added slowly and stirred into the liquid decontaminant (see Section 8 for preparation of decontaminating solution) in an open-top container. Be sure this process is conducted in a well-ventilated area. It is recommended that one part of MDI be added to ten parts of decontaminating solution. Adding the decontaminating solution to the MDI may produce excessive heat. The amount of MDI product treated should not exceed 10% of the amount of decontaminating solution used. Leave the treated drum for 48 hours in a properly ventilated area to allow evolved carbon dioxide to escape. Decant the liquid and dispose of both the liquid and solid material according to all federal, state, and local regulations.

Method 3: Reaction with Waste Polyol
React MDI waste with activated waste polyol to make low quality polyurethane foam which can be sold or used as a manufactured product. If the foam produced is to be disposed, applicable regulations must be followed. In the United States, all foam produced in this manner for disposal is classified as "Non-Hazardous Waste," regulated under RCRA. This method should only be used when a correct stoichiometric mixing can be guaranteed. Improper mixing will leave a product containing unreacted MDI or polyol. In general, if intended for disposal, this is a less desirable method for use due to the large volume of foam produced. ***Caution****: The MDI/polyol reaction is exothermic, which may cause spontaneous combustion.*

Decontamination and Disposal of Used Containers
MDI products may be delivered in drums. These drums are designed to be one-way packages and cannot be returned to the suppliers.

Residual MDI product will remain in the drum until it has been completely emptied. Local and federal regulations vary concerning the disposal of empty containers. Empty MDI drums are potentially hazardous and should therefore only be handled by trained personnel. Personnel should be trained to empty MDI drums completely. Residual MDI product may remain in the drum after proper draining (this residual must be 0.1-2.0 kilograms, or less than one inch depending on product and drum type, to be considered “empty” by RCRA standards). All MDI drums, after being well drained, should be decontaminated with a prepared decontaminating solution using the following procedure:

a) Spray or pour 5 - 30 liters (2 to 8 gallons) of decontaminating solution into the drum, making sure the walls are well rinsed. This can be achieved by use of a spray head or by rolling the drum for several minutes. The use of high-pressure spray equipment can significantly improve the speed and effectiveness of drum cleaning.

b) Leave drum standing unsealed for at least 48 hours to allow complete reaction. Sealing of the drum must be avoided to prevent pressure buildup by evolved CO_2.

c) Pour out liquid decontaminant into a storage vessel. The decontaminating solution can be used several times. There are, however, disadvantages to using this method. The resulting crust can conceal unreacted diisocyanate, especially in the case of drums not having been adequately drained. It is also difficult to remove the crust from the walls of the drum.

This procedure is required to assist reconditioning firms and is often mandatory for the acceptance of the waste drums for reconditioning. Only after proper cleaning can drums be recycled or scrapped without any hazard. In most countries, organizations of drum scrappers have been formed. They should be consulted for details concerning the collection and reprocessing of both cleaned and uncleaned MDI drums.

If decontaminated drums are to be disposed of, they should be punctured to prevent reuse. Independent of the method used, cleaned MDI drums must not be used for the storage of food or animal fodder.

All local and federal regulations must be complied with when cleaning and disposing of empty MDI drums.

Some nations allow well-drained drums to be sent to a permitted re-conditioner without being decontaminated. If this is allowed, the empty drums must be labeled analogous to the filled drums and all closures must be tight to prevent water contamination. Water contamination can cause CO2 gas to be evolved, which could pressurize the drum and create a serious hazard.

Under no circumstances should empty MDI drums be burned or cut open with a gas or electric torch, as toxic decomposition products may be liberated.

Ecological Effects
Ecotoxicology investigations to date have shown that MDI products are not appreciably toxic to fish, bacteria, and invertebrates (LC_{50}>100 mg/L) or to worms and plants (LC/EC_{50}≥1,000 mg/L).

The reaction products of MDI and water are not biodegradable but are chemically inert. See References: MDI Transportation Guidelines, CPI (2002)

10. Frequently Asked Questions

1. What are the standards for unloading bulk MDI from truck or rail?
The operation of unloading (or loading) any tank truck, iso tank container, tank car, or small container of MDI is potentially hazardous. Unloading facilities must be designed and located giving due regard to the potential hazards of MDI products.

Written operating procedures covering all aspects of the unloading operation of MDI products must be prepared and available to all involved parties. All necessary PPE and emergency equipment must be available for the unloading operations. Personnel must be trained in correct use of all protective clothing and emergency equipment (see Section 5).

Unloading of MDI products from bulk containers should be performed with a self-priming, seal-less pump and a vapor return line connected between the storage tank and the bulk delivery container. The seal-less design eliminates potential seal failure. Due to the MMDI freezing point, MMDI transfer lines must be heated. Dry air or nitrogen must be available to purge the unloading lines and vapor return line after unloading is completed. The storage tank must be equipped with a high-level device which will stop the unloading automatically if the maximum tank level is reached.

If dry air or nitrogen pressure is used to transfer MDI products from a bulk container to the storage tank, the pressure must be regulated below the maximum safe operating pressure of the bulk container, and the storage tank vent must be sized accordingly. After disconnecting hoses, all exposed fittings and hoses must be protected with caps or plugs.

The dimensions and physical arrangement of bulk containers vary. Contact your local BASF office for unloading instructions on specific container types.

2. Can MDI be stored in an outdoor bulk storage tank?
Yes, but the tank should be insulated, have a heating source if necessary (e.g., heating jacket, heating coils, or heat exchanger), and a top mounted agitator to avoid local overheating if necessary. All MDI storage tanks should be located above ground and be certified for positive pressure for unloading or if contamination occurs. Storage tanks are recommended to be placed indoors for spill containment and to prevent the effects of weather variation on the product.

3. What occurs during an isocyanate reaction with water?
The reaction of isocyanates with water 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.

4. Do you need a nitrogen pad for an MDI bulk storage tank?
MDI storage tanks should be blanketed with dry air or nitrogen (-40°F/°C dew point). Storage tanks should be maintained under slight positive pressure (1 mbar) and should be pressure-controlled by nitrogen or dried air. Storage tank vents must be sized to adequately protect the tank against pressure buildup during unloading operations or the generation of pressure from moisture contamination. Storage tank ventilation can be accomplished by pressure control through an activated carbon filter or knockout pots.

5. What do you do if someone is sprayed with MDI?
Immediately move the affected person to a safety shower or other source of large amounts of water. Remove all contaminated clothing while under the shower and thoroughly wash affected areas with soap and water or polypropylene glycol. Medical treatment should be given if skin irritation persists (e.g., redness, swelling, or burning sensation). Soak contaminated clothing in decontaminating solution and launder before reusing or destroy in cases of severe contamination. Take precautions against additional exposure when completing these activities.

6. What do you do if MDI is ingested?
If MDI is ingested immediately contact the Human Poison Control Center (1-800-222-1222). The affected person should immediately drink large amounts of water to reduce the concentration of the chemical. Vomiting should not be induced. Keep the individual calm and protect against loss of body heat. The person should be transported to a medical facility as quickly as possible. If vomiting should occur, more water should be given immediately. Never give fluids or induce vomiting if the person is unconscious or having convulsions.

7. What do you do in the event of an MDI spill?
Perform the following steps in response to an MDI release.

a. Evacuate nonessential personnel from the area
b. Notify emergency centers and management if required
c. Use proper protective equipment
d. Contain spill
e. Transfer spilled MDI to open container using pump or absorbent material
f. Neutralize spilled MDI
g. Decontaminate surfaces
h. Isolate/dispose of waste
i. Monitor for residual diisocyanate
j. Perform additional decontamination if diisocyanate is detected

Depending upon the size, location, and type of release, government agencies or authorities may require notification. In the United States, any release of over 5,000 lbs. to the environment must be reported to the NRC (1-800-424-8802) and the local planning commission as outlined under EPCRA regulations. Transportation incidents involving MDI must be reported to the NRC for any release over the reportable quantity of 5,000 lbs. (approximately 500 gallons). This is a requirement of U.S. Federal CERCLA regulations.

For transportation incidents in Canada, Transport Canada operates Canutec.
Transportation incidents in Canada should be reported to Canutec (1-613-996-6666).

8. What do you do if your MDI drums are bulging?
A bulging drum of MDI should be assumed to be the result of contamination, usually with water. This slow but unstoppable reaction with a diisocyanate produces CO_2, which increases the pressure inside the container. Since it is not easy to judge the acute risk of bursting, the drum under pressure should not be moved. A tarpaulin should be placed over the drum.

It is necessary to relieve this pressure safely before the drum bursts. This is best accomplished by puncturing the top of the drum with a long-handled spike. Some response companies have specialized drum de-pressurization devices. During this action, all uninvolved persons must be removed from the area and the working personnel must use complete chemical protection. The punctured drum must then be placed in an oversized drum with pressure venting capabilities. It must be remembered that the original contamination will probably continue to cause a pressure increase. The container must be regularly vented using proper safety precautions and BASF contacted for disposal recommendations.

9. Does BASF have a recommended Piping & Instrumentation Diagram for the design of isocyanate bulk storage?
No. There is no specific layout or equipment design that must be used for isocyanate bulk storage. Multiple options are possible and should be evaluated as part of a standard engineering design process.

10. What products should be stored in a warm room? At what temperatures?
The recommended storage temperature of MDI products depends on the composition. The most favorable storage temperature for PMDI products is 68 to 86°F (20 to 30°C). MMDI products may be stored in solid or liquid form, and the storage temperature is strongly dependent on the product. Refer to the Technical Data Sheets for each product for information concerning the optimum storage temperature.

11. Why does my MDI product appear cloudy?
There are several reasons why an MDI product may appear cloudy. The product may be old and may have exceeded its shelf-life. Over time, some MDI products will form increasing amounts of dimeric species (uretdiones), often referred to as “dimer.” MDI dimer has limited solubility in the product and, at some point, the level of dimer may exceed its saturation point. When this occurs, the dimer will begin to precipitate out of solution, causing the product to become cloudy. After extended periods of time, the dimer may even begin to settle out of solution at the bottom of the container as a fine white solid.

Other causes of cloudiness in the product include contamination by water or other foreign chemicals. Some MDI products, mostly those with high monomeric MDI content, especially 4,4’- MDI, are very sensitive to contamination by small amounts of water. Sometimes even exposure to humidity in the air in the headspace above some product may eventually cause the product to become cloudy. The cloudiness is caused by the reaction of small amounts of humidity with MDI, primarily 4,4’-MDI, which results in the formation of MDI urea species. These MDI ureas have limited solubility in the product, causing the product to appear cloudy. At higher concentrations these MDI ureas may even precipitate out of solution as white solids.

Certain chemicals, solids or liquids, may have limited solubility or compatibility in MDI products. Thus, contamination with these chemicals, even in small amounts, may cause the MDI product to appear cloudy. Other chemicals may be completely compatible with MDI but may react with MDI to form products that are incompatible, resulting in a cloudy appearance.

12. My MDI shipment is a different color than usual. Is there a problem with it?
If the product contains PMDI, the color may range from light amber to dark brown, depending on the composition. PMDI is manufactured in a highly energetic process, using extremely reactive reagents. As a result, varying amounts of color bodies are formed in the process. These color bodies could come from extremely small amounts of contaminants in the raw materials used to make PMDI or could be inherent in the process chemistry. The concentration of these by-products is very low, but since they are highly colored the presence of these by-products causes the final PMDI product to have an appearance ranging from light amber to brown. Batch-to-batch variation may result in slightly more or less of these colored by-products, resulting in some variation in the color of the final product. It is important to realize, however, that these colored species do not, in any way, affect the quality or performance properties of the final polyurethane prepared from the PMDI. In general, if lower color is desired in the final polyurethane, one normally selects products that are based on 100% monomeric MDI, or those that have minimal PMDI content.

Products based on only MMDI typically have colors ranging from water white to yellow. In MMDI products the color arises from very small amounts of by-products formed by the reaction of MDI with other ingredients in the product. The color does not, in any way, affect the quality or performance properties of the final polyurethane prepared from the MDI.

13. What materials are safe to expose to MDI?
MDI reacts with acids, alcohols, basic materials (e.g., sodium hydroxide, ammonia, and amines), magnesium and aluminum (and their alloys), metal salts (e.g., tin, iron, aluminum, and zinc chlorides), strong oxidizing agents (e.g., bleach and chlorine), polyols, and water (CPI, July 2003). These reactions may be violent, generating heat, which can result in an increased evolution of isocyanate vapor and/or a buildup of pressure within closed containers.

Tanks may be fabricated of unlined carbon steel. The steel tanks should be rust-free because trace iron contamination may affect the MDI reactivity. Other satisfactory materials include stainless steel, glass-lined steel, or nickel-clad steel; however, these configurations are more expensive. Stainless steel is the recommended material of construction for pumps, discharge pipelines, and valves. MDI is not generally corrosive towards metals or other materials at room temperature, but the presence of a small amount of acidity in PMDI can produce some corrosion with copper alloys and aluminum. Copper, zinc, or their alloys must be avoided as they may cause product deterioration. MDI will attack and embrittle many plastic and rubber materials in a short time, which may cause these materials to crack. Flex Hose must be Teflon®-lined or specially sold and labeled for isocyanate handling.

14. My product has exceeded its recommended shelf life. Can I still use it in my process? The shelf life or storage lifetime of MDI products vary with composition. Refer to the Technical Data Sheets for each product for information concerning shelf life. Many MDI products, however, will be usable well beyond the shelf life stated in the Technical Data Sheets. Customers with appropriate analytical capabilities can verify that a product is still good to use by re-running its specifications. If the specifications are still within the ranges indicated on the products Certificate of Analysis (COA), then the product can still be used. Customers without the appropriate analytical capabilities may contact their distributor or their BASF salesperson to request recertification of their product.

15. My product froze and contains a large amount of white solid material. Can the product be "melted" again? What should I do?
When some MDI products are exposed to temperatures lower than those recommended in the Technical Data Sheets for that specific product, the product "freezes". When a product freezes monomeric MDI (primarily 4,4'-MDI) crystallizes out of solution as a white solid. The ease at which a product freezes when subjected to low temperatures depends on its composition. Typically, product containing high levels of monomeric MDI, especially 4,4'-MDI, tends to freeze more readily.

When an MDI product freezes, sometimes warming the product to warm room temperature (75 to 85ºF or 24 to 29ºC) is all that is required to melt the MDI crystals and result in a clear product. Other MDI products need to be warmed to higher temperatures, 110 to 122ºF (43 to 50ºC), to melt all the MDI crystals. Other products, however, are more sensitive and even when heated to 110 to 122ºF, some undissolved white solids may remain on the bottom of the container. These insoluble white solids are MDI dimers, and once formed cannot be dissolved back into solution. They can only be removed by filtering the product.

The tendency to form insoluble MDI dimer increases with time after a product freezes. Therefore, it is important not to keep an MDI product frozen for a long period of time. If a product shows evidence of freezing, after exposure to temperatures lower than that recommended in the Technical Data Sheets, it is best to immediately warm the product to either warm room temperature (75 to 85ºF), or higher temperatures (110 to 122ºF). In many cases, prompt warming to melt the MDI crystals will result in a clear product that can be used without any change in performance properties.

11. References

Equipment Guidelines for Diisocyanate Storage Tanks
This Technical Bulletin is intended to provide guidelines for describing various equipment options for storage tank systems intended for diisocyanate product service. The bulletin includes a reference table of equipment options, which is supplemented by additional text. (AX-365, 2018)

Uniform Hazardous Waste Manifest
This document provides information on the U.S. Environmental Protection Agency (EPA) Uniform Hazardous Waste Manifest. EPA requires hazardous waste generators and transporters to use the Uniform Hazardous Waste Manifest for all hazardous waste shipments, including waste MDI, which is a listed hazardous waste (U223). (AX-406, 2013)

Health Effects of Diisocyanates: Guidance for Medical Personnel
This guidance document is designed specifically for medical personnel to provide current information about the potential health effects from diisocyanate exposure, and to provide guidance to assist with medical diagnosis and management. The discussion focuses on two widely used diisocyanate-based products: diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI). (AX-150, 2013)

Occupational Hygiene Air Monitoring for MDI and TDI Guidance
This guidance document describes workplace air monitoring methods for MDI and TDI and provides information on personal and area sample collection. Several instruments and derivatization methods for monitoring vapors are presented. (AX-248, 2012)

MDI Transportation Guidelines
MDI Transportation Guidelines: This 54-page technical guideline provides a summary of regulatory requirements affecting the transport and distribution of MDI, and relevant industry safety guidelines. (AX-198, 2014)

Guidance for Melting 4,4'-Methylene Diphenyl Diisocyanates (MDI) in Drums
This guidance provides information that is intended to serve as a general guideline on how to heat drums to melt frozen or fused MDI. (AX-363, 2012)

Guidance for the Selection of Protective Clothing for MDI Users
Describes useful guidance on selecting the appropriate PPE and the performance characteristics of gloves, coveralls, splash suites, and other protective suites commonly used when working with MDI. (AX-178, 2013)

Guidance for Working with MDI and Polymeric MDI: Things You Should Know
An easy-to-read, brochure which provides information about important health and safety considerations when working with MDI or Polymeric MDI. (AX-205, 2012)

Guidelines for Freight Securement: Freight Loading and Securement for Chemical Shipments in the Polyurethane Industry
This guidance document is intended to provide basic principles and examples of freight loading and securement for intermodal domestic and international shipments. The document is intended for transportation professionals that ship or receive polyurethane related materials. The comprehensive guidance document provides useful and essential safety mechanisms, preload inspection of trailers and containers, restraint systems and the closure of the transport containers. Clear, detailed photographs provide helpful representations of appropriate freight loading and securement practices. This document also references regulatory and modal requirements governing these shipments. (AX-173, 2012)

MDI Emissions Reporting Guidelines for the Polyurethane Industry
(RCAP Program)

Transloading Polymeric Methylene Diphenyl Diisocyanates (PMDI)
These guidelines have been developed to describe various options for transloading PMDI from rail tank cars to cargo tank trailers (AX-409, 2015)

Contact your BASF representative to obtain the following documents:

BASF Isocyanate Medical Guideline - First Aid Providers

BASF Isocyanate Medical Guidelines – Physician

Contact your BASF representative to obtain this document:

A Guide for the Primary Care Physician in Evaluating Diisocyanate Exposed Workers for Occupational Asthma

International Isocynate Institute Reference Materials

MDI & TDI: Safety, Health and the Environment: A Source Book and Practical Guide
http://www.diisocyanates.org/institute-sponsored-book

For more Information please visit the following websites:

American Chemistry Council (ACC)

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

Diisocyanates (DII) Panel: https://dii.americanchemistry.com/

International Isocyanate Institute: http://www.diisocyanates.org/

12. Other Considerations

The regulations for handling MDI and MDI variants as well as other potentially hazardous chemicals are continually evolving. Also, regulations and procedures vary widely from country to country. The body of this publication contains general information for handling MDI and MDI products and is not a substitute for a thorough understanding of your regulatory requirements.

About BASF Polyurethanes

The basic polyurethane chemicals division of BASF provides manufacturers of polyurethane products with a broad catalog of raw materials, innovations, and technical expertise to help our customers advance their technologies in a diverse set of applications across various industries. With facilities in Geismar, LA and Wyandotte, MI, we supply aromatic isocyanates and an array of conventional and graft polyols to many of the major users of polyurethane raw materials, and through a comprehensive network of distributors. Our customers use these building blocks to formulate products in coatings, adhesives, sealants, elastomer (CASE) applications, as well as molded and slab-stock flexible foams, binders for engineered wood products (OSB, MDF, and PB), and polyisocyanurate insulation boards.

For more information, please visit our website at www.polyurethanes.basf.us

Contact:

BASF Corporation
Polyurethane Raw Materials
1609 Biddle Avenue
Wyandotte, MI 48192 USA
tel: 877-297-3322
fax:800-720-1132
e-mail: CMCustomerCare@basf.com
website: **www.polyurethanes.basf.us**

To learn more, scan the QR code.