



ISONATE™ AND PAPI™

Pure, Modified and Polymeric MDI

October 2009

Bulk and Drum Handling & Storage Guide

containment

Storage

Training

Stewardship

Safety

Care

Instructions

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Pure, Modified and Polymeric MDI – ISONATE™, VORANATE™ and PAPI™

Manufacturers and processors of various types of plastics and prepolymers rely on pure, modified and polymeric MDI products from Dow for a variety of applications. This guide describes practices, procedures and potential hazards associated with handling and storing these isocyanates.

What is MDI?

MDI or MMDI (monomeric MDI) is a standard abbreviation for “pure” diphenylmethane diisocyanate, methylene bisphenyl isocyanate, methylene diphenyl diisocyanate or methylene bis (p-phenyl isocyanate).

Other synonyms for MDI are isocyanic acid: p,p'-methylene diphenyl diester; isocyanic acid: methylene di-p-phenylene ester; and 1,1'-methylene bis (isocyanato benzene).

The “polymeric” form of MDI (p-MDI or PMDI) is typically 30 percent to 70 percent diphenylmethane diisocyanate, and the balance is higher-molecular-weight fractions. However, some manufacturers and end users also use MDI to refer to the undistilled mixture of 4,4'-diphenylmethane diisocyanate and higher-molecular-weight fractions.

Dow's family of quality isocyanates – pure, modified and polymeric MDI – includes:

- ISONATE™ pure and modified MDI
- PAPI™ polymeric MDI
- VORANATE™ polymeric MDI
- SPECTRIM™ MDI-based isocyanates
- SPECFLEX™ MDI-based isocyanates
- Other MDI products such as VORACOR™, VORATEC™ and VORAMER™ for formulated systems applications

Pure MDI

Pure MDI may be combined with polyethers, polyesters or other polyols to produce a wide range of products and materials for coatings, elastomers, adhesives and sealants applications including both high- and low-density microcellular foams, fibers, as well as a variety of thermoplastic polymers suitable for extrusion, injection molding and solution applications. Pure MDI is a typical raw material for the production of prepolymer.

Modified MDI

Modified MDI products, such as prepolymers or blends are derived from diphenylmethane diisocyanate. Modified MDI may be combined with long-chain polyethers, polyesters or other polyols, including short-chain diols or triols, to produce a wide range of products and materials, such as adhesives and sealants as well as a variety of thermoplastic polymers suitable for extrusion, injection molding and solution applications.

Polymeric MDI

Polymeric MDI products (polymethylene polyphenylisocyanates, sometimes referred to as p-MDI or PMDI) are derived from the classic chemical reaction of carbonyl-chloride with aniline-formaldehyde condensate.

Polymeric MDI products are well suited for many industrial, manufacturing and specialty end-use applications.

Summary of Safe Handling Information for MDI Products

Pure, modified and polymeric MDI products from Dow are available in non-returnable drums and pails, and in totes and bulk containers.

CAUTION: Pure, modified and polymeric MDI products are potentially hazardous materials that must be shipped, handled and stored with care, consistent with the safety recommendations and precautions outlined on the product labels and described on the Safety Data Sheets (SDSs) as well as this guide.

The recommendations given in this guide are based on the results of numerous tests as well as practical, in-the-field experience, and are believed to be accurate and reliable. However, as the specific circumstances associated with a customer's use of pure, modified and polymeric MDI are unknown to Dow and are beyond its control, Dow cannot guarantee that adhering to these recommendations will ensure absolute safety.

To request Safety Data Sheet (SDS), or to find out more about specific operations and procedures relating to safe handling, shipping, unloading, storage, use or disposal, contact the Dow Customer Information Group (CIG) at relevant number provided on page 52.

Part One – Properties, Handling Precautions, Health Effects and First Aid

Properties

Although the three forms of MDI differ both chemically and physically, they present similar basic risks and require similar approaches to safe handling. Please refer to the relevant safety data sheet for specific information.

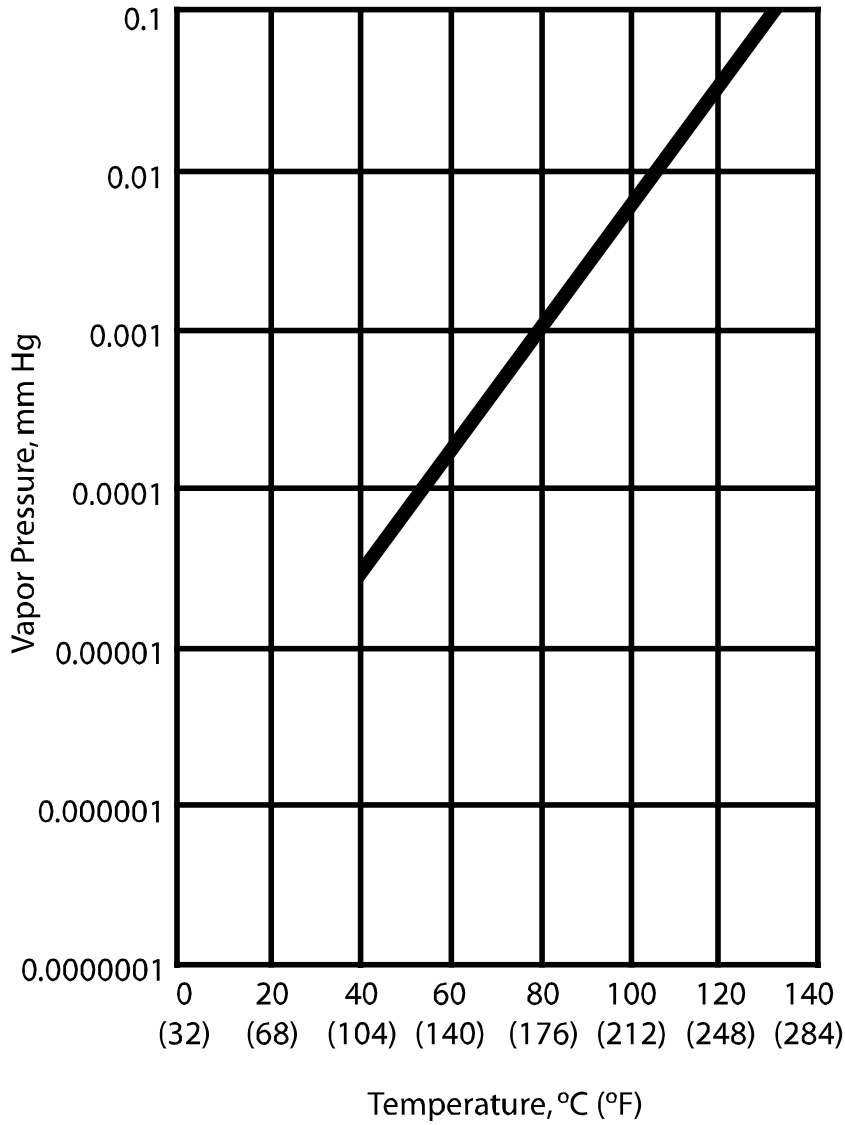
Table 1 and Figures 1 through 4 include the typical physical properties of various forms of MDI.

Table 1: Typical Physical Properties of Pure, Modified and Polymeric MDI			
Properties ¹	Pure	Modified	Polymeric
Molecular Weight	250.27	—	—
Physical State at Room Temperature	Solid	Liquid	Liquid
Color	White to light yellow	White to light yellow	Brown
Density, g/ml	1.180 (43°C)	1.214 -1.221 (25°C)	1.22-1.25 (25°C)
Vapor Pressure, mm Hg @ 25°C	< 10 ⁻⁴ (43°C)	< 10 ⁻⁵	< 10 ⁻⁵
Boiling Point ² , °C (°F)	Decomposes before boiling	Decomposes before boiling	Decomposes before boiling
@ 1 mm Hg, °C (°F)	171 (340)	171 (340)	181 (358)
@ 5 mm Hg, °C (°F)	200 (392)	200 (392)	210 (410)
Flash Point, closed cup, ASTM D 93, °C (°F)	> 177 (> 350)	> 177 (> 350)	> 204 (< 400)
Specific Heat, g-cal/g-°C	0.43	0.43	0.43
Thermal Conductivity, g-cal/cm-sec-°C	0.0003	0.0003	0.0003
Coefficient of Thermal Expansion, m/m-°C	0.0009	0.0009	0.0008
Heat of Vaporization, cal/g	86	86	—
Heat of Fusion, cal/g	32.6	—	—
Vapor Density (air = 1)	8.6	8.6	8.5-8.6
Shelf Life ³ (clear melt without filtration) @ -20°C	~12 months	—	—
@ 25°C	—	6 months	6 months
@ 43°C	25 days	—	—
Max. Airborne Vapor Conc., ppm @ 77°F	0.007	—	—
Melting Point, °C (°F)	38 (100)	—	—
Acidity, % as HCl	< 0.003	< 0.003	< 0.04
Hydrolyzable Chloride, ppm	< 25	—	—
Volatiles by Volume	Nil	Nil	Nil

¹These are typical properties only, and are not to be regarded as sales specifications.
²Decomposes at approximately 230°C (446°F).
³Under recommended storage temperatures and handling conditions.
⁴Temperature ranges between 10°C (50°F) and 37.8 °C (100°F) give erratic dimer growth.

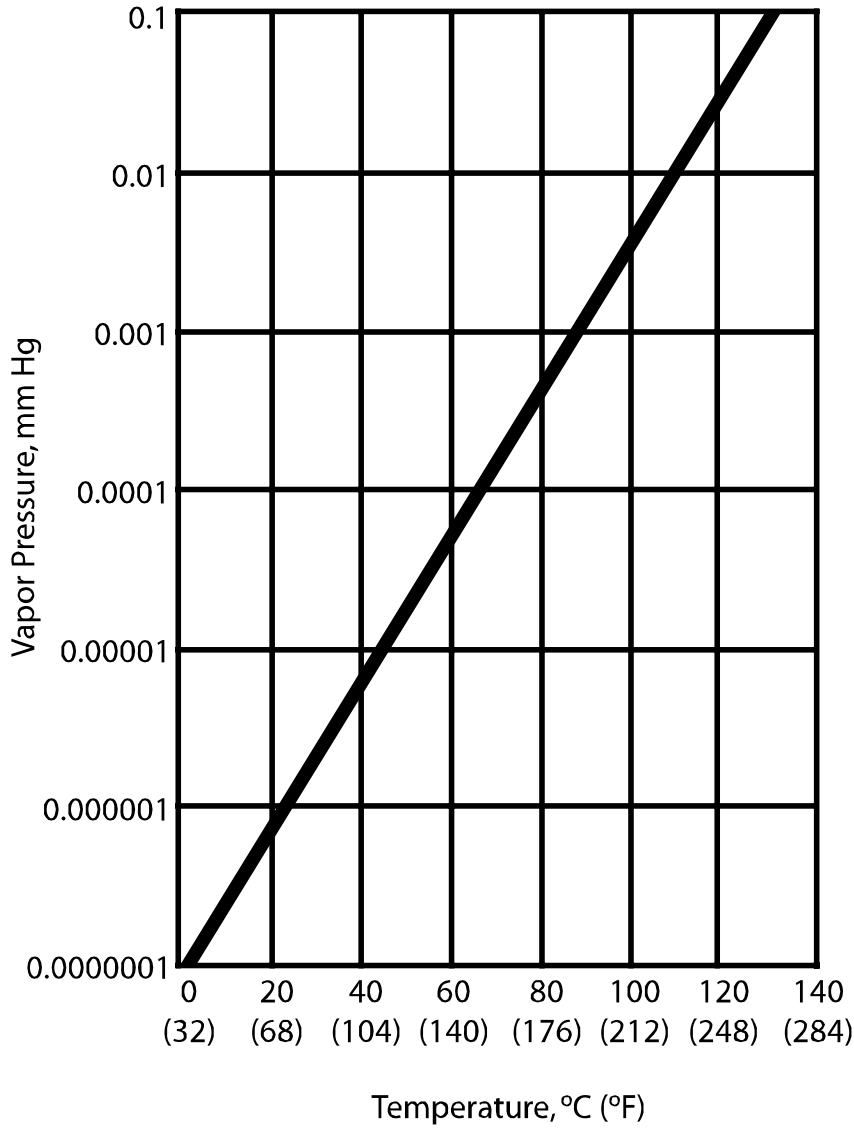
Note: See the appropriate SDS for specific values for each MDI product.

Figure 1: Vapor Pressure of Pure MDI 4-4' MDI



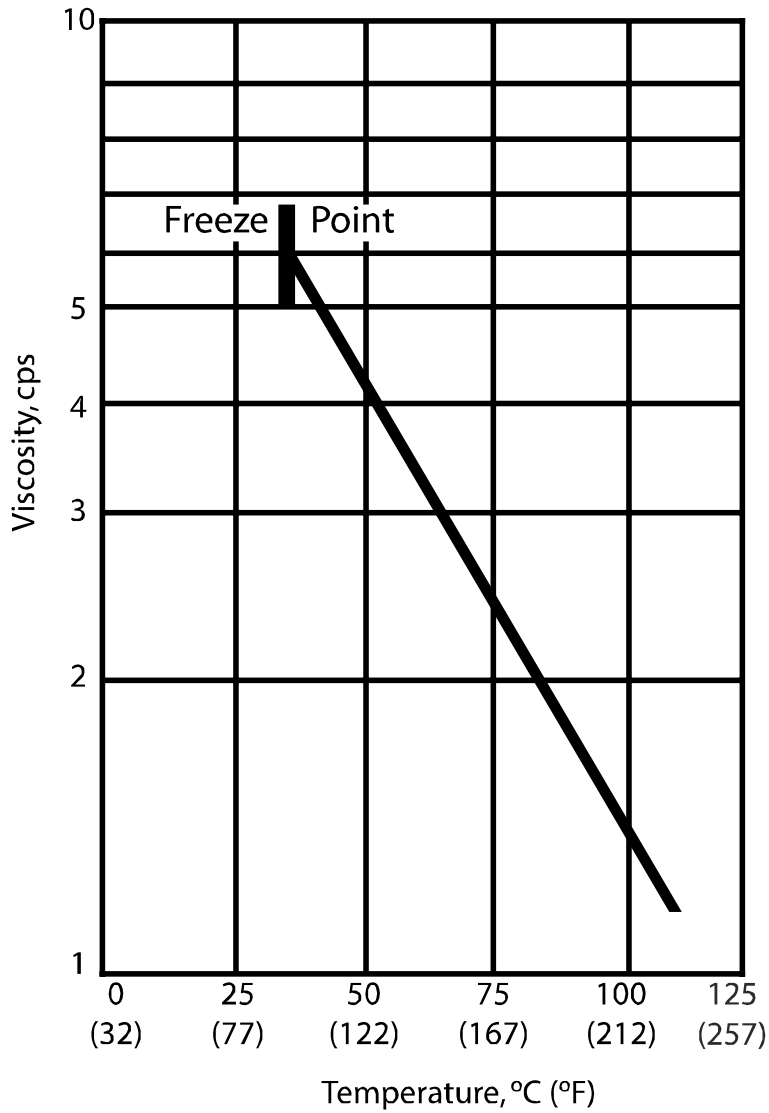
Note: These are typical properties only and are not to be regarded as sales specifications.

Figure 2: Vapor Pressure of Polymeric MDI



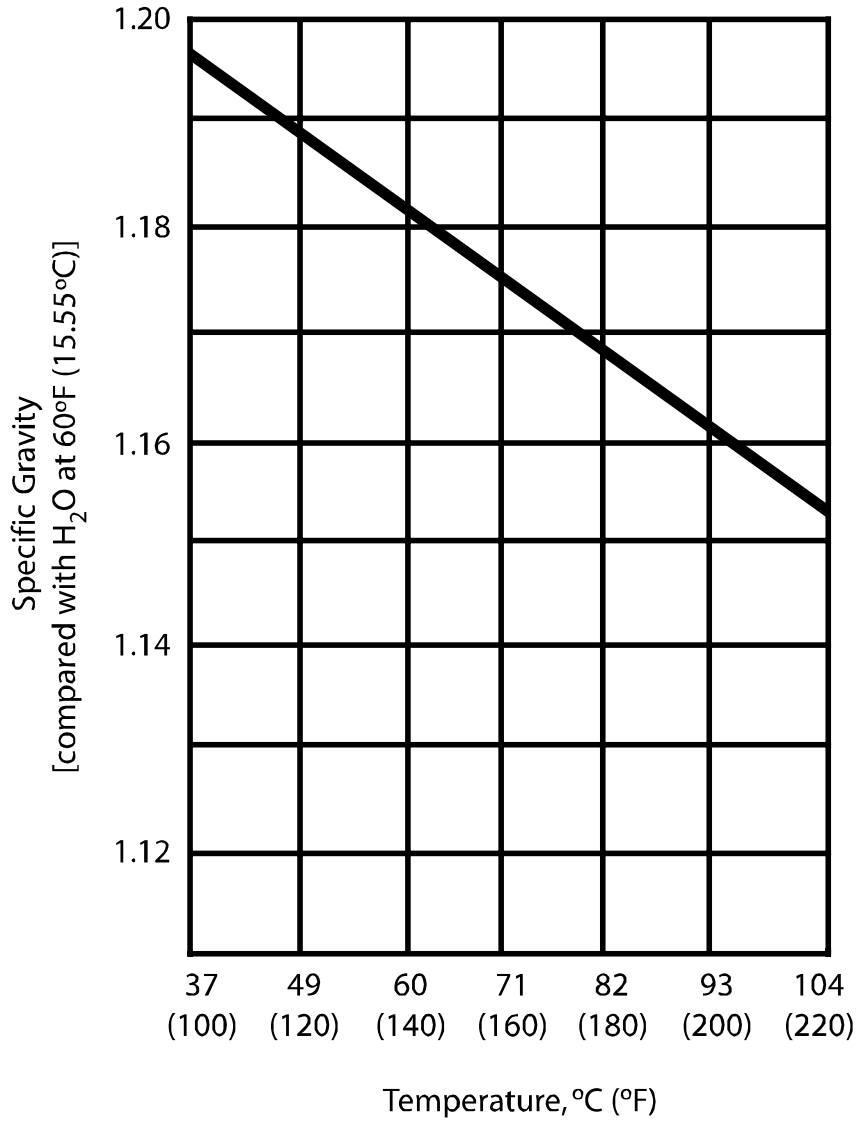
Note: These are typical properties only and are not to be regarded as sales specifications.

Figure 3: Viscosity of Pure MDI 4-4' MDI



Note: These are typical properties only and are not to be regarded as sales specifications.

Figure 4: Specific Gravity vs. Temperature for Pure MDI 4-4' MDI



Note: These are typical properties only and are not to be regarded as sales specifications.

NOTICE: The information and recommendations that follow are presented in good faith. However, since this information and the recommendations are provided without charge, and since use conditions are not within Dow's control, Dow does not guarantee any results from the use of the information or the recommendations; no warranty, express or implied, is given. It is the Customer's responsibility to determine that its workplace and practices comply with law and applicable safety standards.

Handling Precautions

All personnel should consult the appropriate SDS and understand the safety precautions in this guide before using any MDI product.

To protect product quality and minimize the hazards associated with their use, follow the recommended guidelines listed below.

- Only knowledgeable and experienced personnel should handle and store MDI products.
- Avoid exposing MDI to strong bases or to active hydrogen-containing compounds, such as water, ammonia, amines and alcohols. Exposure to these materials could result in the explosive rupture of restricted lines or closed vessels due to the liberation of heat and/or the generation of carbon dioxide gas.
- Take care to prevent MDI spills and protect from flame. These conditions can lead to the release of potentially harmful concentrations of isocyanate vapors and harmful decomposition/combustion byproducts.

Moisture Control

Water (moisture, humidity) is the most common, hazardous contaminant of any MDI product. At room temperature, water reacts with isocyanates to form both an insoluble urea compound and large quantities of carbon dioxide gas. (This reaction may occur slowly, but heating or agitation may accelerate the reaction.) This insoluble urea derivative will be deposited on the surfaces of the equipment in which it is formed. Lines and orifices can become plugged, thus closing or restricting the vessel, and the liberated carbon dioxide gas can create a serious pressure hazard.

WARNING: Water or moisture contamination can produce sufficient carbon dioxide gas to rupture the container. Elevated temperatures accelerate this reaction.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

Even relatively small amounts of water can cause significant problems. For example, at standard temperature and pressure, as little as one fluid ounce (29.6 ml) of water can release as much as 1.5 cubic feet (40 liters) of carbon dioxide. In a sealed 55-gallon drum (208 liters) that is 95 percent full, 1.5 cubic feet (40 liters) of carbon dioxide could result in pressures of up to 30 psi to 40 psi (2 atm to 3 atm), which would probably rupture the drum. Even if the drum did not rupture from these excessive pressures, removal of the bung could result in isocyanate liquid squirting from the bung opening, endangering the person opening the drum.

To protect MDI from atmospheric moisture, blanket all containers with a dry (-40°C [-40°F] dew point), inert gas pad. Under most conditions, nitrogen is the recommended dry, inert pad or purge gas for these products. The use of dry air is not recommended because oxidation can cause discoloration. Carbon dioxide is soluble in isocyanates and should not be used.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- If MDI products have been or are suspected of having been contaminated with water, do not tightly close vessels containing these products. If contamination is suspected, see the section in this manual labeled "Pressurized Drums," or "Spills and Leaks, – Containment and Cleanup," for further information. When containers have been opened for sampling, inspection or partial withdrawal, re-blanket the containers with a pad of dry nitrogen.
- Carefully clean and dry equipment and containers to be used, then purge with dry, inert gas. The purge gas, in addition to being moisture free, must also be free of oil and rust. Thus, filter traps should be installed in the gas lines to remove these and other contaminants.
- For small installations, manifold cylinders of dry nitrogen arranged into banks may be adequate. However, larger installations may call for a nitrogen generator or a tie-in to existing plant inert gas systems.
- If plant air must be used (Note: air is not recommended because it contains oxygen), purification equipment such as oil traps, a bauxite absorber to keep oil out of the drying beds, and an air dryer should be installed between the compressor and the isocyanate system, and properly maintained. When using a desiccant-type air dryer in conjunction with an air compressor, lower the temperature of the air before entry into the air dryer. Hot air may purge the moisture from the desiccant and force it through to the product. An entrainment separator ("knock-out pot") should be added between the cooler and the air dryer. Also, a final filter and a back-pressure regulator should be fitted directly in front of the isocyanate system.
- Instruments for detecting the failure of the drying equipment for the purge gas are required when large quantities of isocyanate are handled and stored. Several different moisture-detecting instruments are commercially available.
- When lines leading to and from storage tanks are not in use, they should be tightly capped to prevent moisture from coming in contact with residual product left in the lines. Also, all flexible connection lines should be rinsed with a suitable dry solvent.¹ These fittings should be dried and stored in a dry place.

¹ Do not use alcohols due to risk of chemical reaction. The use of solvents entails additional risks of flammability and toxicity. Therefore, such materials should be used in strict accordance with supplier recommendations for safe handling.

(A plastic bag containing a desiccant, such as silica gel, makes a convenient, portable, dry place for storing such items.)

Temperature Control

Storage personnel should check current SDS, technical data sheets and/or other appropriate publications for the recommended storage temperatures for each of the various MDI products. Prolonged storage of MDI products at temperatures significantly higher or lower than those recommended may lead to product deterioration, including dimer formation.

Table 2: Storage temperatures of MDI products (°C)

Product Family	Storage
Polymeric MDI viscosity > 150 mPa.s	15-45°C, preferably 24-35°C*
Modified MDI/prepolymer/polymeric MDI with high MMDI content and viscosity < 150 mPa.s	24-40°C, preferably 25-35°C*
Pure MDI delivered as liquid (all products except pure MDI products with ortho-para (o-p') content above 45%)	41-48°C, preferably 41-45°C
Pure MDI delivered in frozen form	Below -15°C, preferable below -18°C*

*For maximizing shelf life

Table 3: Storage temperatures of MDI products (°F)

Product Family	Storage
Polymeric MDI viscosity > 150 mPa.s	59-113°F, preferably 75-95°F*
Modified MDI/prepolymer/polymeric MDI with high MMDI content and viscosity < 150 mPa.s	75-104°F, preferably 77-95°F*
Pure MDI delivered as liquid (all products except pure MDI products with ortho-para (o-p') content above 45%)	106-118°F, preferably 106-113°F
Pure MDI delivered in frozen form	Below 5°F, preferable below 0°F*

*For maximizing shelf life

Consult your Dow representative for further information or specific needs on temperature control.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- Although there is little danger of crystallization or separation during freezing for most polymeric isocyanates, there are some specific exceptions (refer to technical data sheets and/or SDS for specific details). When any of the polymeric MDI products freeze, the 4,4'-diphenylmethane diisocyanate or MDI portion will crystallize. These products will then exhibit the same dimerization characteristics as pure MDI.
- “Frozen” or crystallized drum shipments should be unloaded promptly and the drums transferred to a properly equipped heating or melting facility. Unless prompt action is taken to reform the original solution, subsequent dimerization will proceed and deteriorate both the clarity and assay of the product. If crystallized material is stored at room temperature without proper heating, high solids formation will result, product will degrade (high dimer formation) and shelf life will be reduced. Also, exposure to low temperature will increase the viscosity of the product and make it difficult to process. However, crystallized product may be recovered by immediate heating to temperatures around 50 – 55 °C (122 - 131°F) and mixing, then cooling to normal storage temperature. The product should be immediately used to avoid further reduction of shelf life.
- The preferred method for rapid and thorough melting of “frozen” or crystallized MDI in drums is slow “drum rolling” (5 rpm to 10 rpm) in atmospheric steam, usually for four to five hours, depending upon the original temperature of the material in the drum. The advantage of this method is that it can melt the product without heating the contents much beyond 65°C (149°F), the point at which dimer formation will begin to increase significantly. Any “drum rolling” operation must be monitored to prevent damage to the drum. For more details, a good industry reference is available via the Center for the Polyurethanes Industry Association.

CAUTION: If MDI has been exposed to significant atmospheric moisture, irreversible changes will occur and restoring the product to its original quality will be impossible.

WARNING: Any drum suspected of being moisture-contaminated should not be heated or rolled. (For additional information on heating and drum rolling, see “Shipment, Handling and Storage,” page 34.)

- If the product is not to be used either immediately or shortly after heating, the drums should be placed in a “retaining oven” or other storage facility designed to keep the contents at the recommended temperature. (For additional information on storage temperatures, see “Shipment, Handling and Storage,” page 34.)
- Do not store polymeric MDI products outside recommended storage temperature range (Tables 2 and 3) as dimerization may occur, leading to increases in viscosity with concurrent decreases in percent NCO. At still higher temperatures (above 160°C [320°F]), MDI will trimerize in an exothermic reaction to form

isocyanurates. This reaction may furnish enough heat to increase product temperature to 204°C (400°F), which will cause the formation of carbodiimides and the subsequent formation of carbon dioxide gas that, in a closed or restricted vessel, could lead to an explosive rupture.

CAUTION: MDI products will slowly begin to decompose beginning at >230°C (>446°F) and at higher temperatures, decomposition can progress extremely rapidly. MDI products should never be exposed to such temperatures.

Contamination by Strong Bases

The presence of strong bases – even in small amounts – can cause any isocyanate to react with itself to form isocyanurates and carbodiimides. The carbodiimide formation is accompanied by the liberation of carbon dioxide, which may present a pressure hazard.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- Avoid any contact between isocyanates and strong bases, such as sodium or potassium hydroxide or alkoxides. Such compounds catalyze the rapid formation of isocyanurates and carbodiimides. Normally, the trimerization reaction occurs first, furnishing heat to cause the carbodiimide reaction to occur. This second reaction liberates carbon dioxide and forms a hard solid or foam that can only be removed from the vessel or line by mechanical means.

WARNING: The liberation of carbon dioxide in a tightly closed or restricted vessel may result in an explosive rupture.

- Industrial cleaning agents are common sources of contamination by strong bases. Do not use or permit the use of sodium or potassium hydroxide or other strong bases in the cleaning of lines or vessels.

Contamination by Amines and Other Active Hydrogen-Containing Compounds

The primary dangers of contamination by amines and other active hydrogen-containing compounds are unintended reactions and the liberation of heat.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- Avoid contamination of MDI products by such compounds as alcohols, glycols, polyols, phenols, amines, amides and acid anhydrides. These compounds will react readily with isocyanates to form their

corresponding addition products. Although reactions caused by contamination from amines or other active hydrogen-containing compounds do not release a gas, they do release considerable quantities of heat, which could ultimately lead to the homopolymerization of the isocyanate to carbodiimides, with a concurrent release of carbon dioxide that will cause pressure. A common form of contamination, typically occurring during unloading or the manufacturing process, is crossover of polyol resin mixtures containing catalysts and solvents and blowing agent (pressure build-up).

- In the event of gross contamination, the exothermic reaction could sharply increase the temperature of the mixture. This could result in the secondary reaction of trimerization, an exothermic process that, in turn, could raise the temperature of the mixture to extremely high levels (explained in a previous section). At this temperature, another secondary reaction – the homopolymerization of the isocyanate to carbodiimides – can occur with a concurrent release of carbon dioxide. Finally, the release of carbon dioxide, especially in a closed or restricted vessel, could lead to an explosive rupture.

CAUTION: If MDI has been contaminated, irreversible changes may have occurred and restoring the product to its original quality will be impossible. Do not add any reagent to try to stop any reaction with the contaminant. Safe disposal of contaminated product is recommended.

Fire and Explosion Hazards

The flash point, by ASTM D93 (P.M.C.C.), of MDI products is >177°C to >204°C (>350°F to >399°F). (See physical properties table.) However, in the presence of oxygen and fire or a heat source sufficient to cause vaporization of the liquid, MDI products will burn. Although MDI does not vaporize readily, there is reason to believe that explosive limits could be reached under fire conditions.

Explosive limits for MDI vapor have not been determined.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products. The current local safety data sheet and National Fire Protection Association (NFPA) emergency response guidebook are good reference documents. It is important to comply with all local, state, provincial and national regulations – many industry association references are provided at the end of this document.

- Under fire conditions, isocyanates will generate irritating and hazardous isocyanate vapors and other hazardous fumes. Thus, firefighting personnel must wear an approved² positive-pressure, self-contained breathing apparatus and full protective clothing including footwear, helmet and gloves. Downwind personnel must be evacuated.
- In the event of a fire involving MDI, use carbon dioxide, foam or a dry chemical extinguisher. For fires covering large areas, alcohol-resistant foams are preferred. General-purpose synthetic foams or protein foams may function, but less effectively. Keep out of low areas where gases (fumes) can accumulate.

Water is not recommended, but may be applied in very large quantities as a fine spray when other extinguishing agents are not available. Do not use direct water stream as it may spread the fire. The reaction between water and isocyanate may be vigorous if the MDI is hot and stirred. When spraying water, be careful not to spread any leaked or spilled MDI. Contain water run-off if possible. Also, once the fire is out, promptly clean up any leaked or spilled MDI. (See "Spills and Leaks – Containment and Cleanup," page 19).

- Do not reseal contaminated containers. A chemical reaction generating carbon dioxide gas pressure may occur resulting in rupture of the container. The reaction forming carbon dioxide accelerates as temperature increases. Dense smoke is emitted when isocyanates are burned without sufficient oxygen. When using water spray in tank-type scenarios (not spills), boil-over can occur when the product temperature reaches the boiling point of water.

Spills and Leaks – Containment and Cleanup

Minor and Large Spills

In considering the various aspects of spills, it is necessary to distinguish between minor incidents, such as those that may occur in a laboratory or workshop regularly handling isocyanates, and large spills that involve, for example, a storage tank or tank truck. Perhaps the most important criterion for distinguishing between the two is the ability of personnel on the scene to deal with the occurrence, rather than the actual scale of the incident.

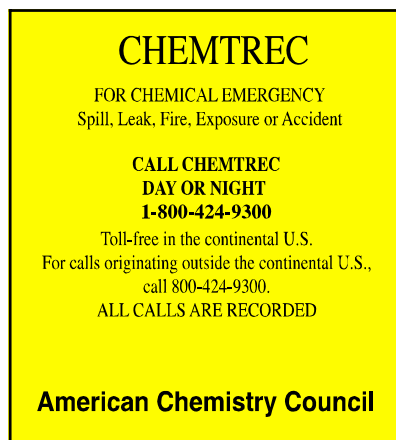
A "minor" spill could be defined as one that can be dealt with using existing equipment and personnel. A "large" spill may be one that necessitates summoning outside assistance from the supplier, police, fire services or other emergency response personnel. Minor spills are potentially as hazardous as large spills if they are not handled correctly.

² In the United States, the authority for approving or certifying respirators is held jointly by the National Institute for Occupational Safety and Health (NIOSH) and the Mine Safety and Health Administration (MSHA). For current information on the status of approvals of respirators, e-mail NIOSH at pubstaf@cdc.gov, or call 1-800-356-4674. Another source for information is the Occupational Safety and Health Administration (OSHA) Respiratory Protection Standard 29CFR 1910.134. (In Canada, refer to the Canadian Standards Association (CSA) standard "Selection, Care and Use of Respirators," Z94.4). In the EU, CE Marking on a product is a manufacturer's declaration that the product complies with the **essential requirements** of the relevant European health, safety and environmental protection legislation – consult current, local language SDS for respirator references.

In the event of a spill that might be considered a “large” spill, call Dow’s Distribution and Emergency Response Center in Freeport, Texas, at 1-979-238-2112, or CHEMTREC for transportation spills at 1-800-424-9300. Call these numbers at any time – day or night – for advice and/or assistance in containing or cleaning up spills and leaks of any size. (See “Large Spills,” page 22.)

For emergency situations in Europe, the ISOPA website provides useful information such as emergency response numbers and focal points for countries.

For other global regions, please refer the local jurisdictional Safety Data Sheet for emergency contact numbers.



Liquid Spills

Although pure MDI-based isocyanates will freeze (begin to solidify) at temperatures <18°C (65°F), all polymeric and most modified polymeric MDI products will remain in liquid form at room temperature (i.e., 22°C [72°F]) and can spill. Careful handling is needed to prevent accidental spills and leaks. (See “Solidified Spills,” page 24.)

- Spills of pure MDI will freeze at approximately 38°C (100°F), but other spills or leaks of “hot” material may remain liquid or solidify slowly if the ambient temperature is high.
- Spills or leaks of MDI should be contained and cleaned up by properly trained and equipped personnel only – all others should leave the contaminated area promptly.
- Protective equipment could include a respirator or air-supplied respirator (for example, a positive-pressure, self-contained breathing apparatus), impervious clothing, footwear and gloves. Selection of specific items will depend on the operation.

Minor Spills and Leaks – Neutralization Procedure

All minor spills and leaks should be contained immediately (e.g., by diking with an absorbent material) to prevent further contamination of the surrounding area.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- Always have a sufficient quantity of inert absorbent material available, such as vermiculite, dirt, sand, clay. Avoid materials such as cement powder.
- Ventilate the contaminated area. Open all doors and windows. To avoid inhaling the vapors of either isocyanate or the decontamination byproducts, workers should wear appropriate personal protective equipment (reference your current, local language SDS).
- If necessary, dike the spill with sand, absorbent clays, etc. If there are standing pools of MDI, the liquid may be pumped (using a drum pump or similar equipment) into a closed-top but not sealed container for disposal (see "Disposal," page 25). Any equipment and containers used must be clean and dry. Properly decontaminate all equipment after use.
- If the source of the leak is a damaged or leaking drum, it should be moved to an isolated, well-ventilated area and the contents carefully transferred to other suitable, leak-free containers. The damaged drum or container should be decontaminated and destroyed. Also, the new container should be blanketed with a dry gas pad (see "Moisture Control," page 13) and then carefully monitored to ensure that atmospheric moisture does not cause over-pressurization.
- After any needed diking (with absorbent) is finished and any liquid pools have been recovered, promptly cover the leak or spill completely with plenty of dry absorbent material. The material should then be shoveled into a suitable container (e.g., metal or plastic drum, poly-lined fiber pack) and removed to a location where the neutralization process can be safely completed. Fill container only half full to allow for expansion. Using appropriate container and disposal procedures is important to handle exotherm generated by the neutralization process.
- Attempt to neutralize by using a suitable decontaminant solution:
 - Formulation 1: sodium carbonate 5-10 percent; liquid detergent (soap solution) 0.2-2 percent; water to make 100 percent.
 - Formulation 2: concentrated ammonia solution 3-8 percent; liquid detergent (soap solution) 0.2-2 percent; water to make 100 percent.

CAUTION: If ammonia solution is used, use good ventilation to prevent vapor exposure. Ensure that the decontaminating solution does not freeze and can be readily used if needed in cold weather conditions.

- For more effective coverage, and to ensure greater contact between the absorbent and the isocyanate, use an industrial-type, heavy-duty broom to sweep the absorbent into the spill. After sweeping, wrap the broom carefully in plastic to contain the isocyanate. Dispose of the wrapped broom properly (one method is incineration). When disposing of any wastes, be sure all applicable regulations are met.
- Shovel the absorbent/isocyanate mixture into an open-top container; fill the container no more than half full. Cover to prevent spills of the absorbent, but do not make pressure tight. Remove the container to a safe disposal site, away from the operating area, to complete the container neutralization reaction. Add neutralizing solution to the isocyanate. The neutralization reaction produces carbon dioxide, so it is important not to close the containers tightly to avoid explosive rupture due to gas pressure.
- The open-top containers should stand undisturbed for at least 48 hours to allow complete neutralization. Exothermic reaction may result in drum melting if exothermic reaction is not finished. Ensure that there is appropriate ventilation around drums.
- After standing for 48 hours, the container may be closed (though not pressure tight) and properly disposed of. (See "Disposal," page 25).
- Immediately after shoveling the absorbent/MDI mixture from the floor, complete the decontamination by mopping the floor with one of the decontamination formulations listed above, allowing the solution to stand for at least 10 minutes. Be sure the area is well ventilated, both during and after cleanup.
- As a precaution, carefully test the atmosphere for residual isocyanate vapor. Instruments designed for MDI monitoring are commercially available. Examples of direct readings instruments that may be used for the detection of MDI include the SafeAir direct reading colorimetric badge (Morphix Technologies), the Sure Spot Active Sampler (Scott Instruments) and the NextStep Isocyanate gas monitor (Scott Instruments).
- When safe working conditions have been re-established, remove and decontaminate or dispose of protective equipment and return to normal operation.

Large Spills

CAUTION: Decontamination and cleanup of major spills can be a complex and hazardous operation, and all the details and operating procedures are not outlined here. Local emergency crews and trained personnel should be called to handle large spills.

In the event of a large spill, a state of emergency should be declared for the affected area. This usually requires the involvement and close cooperation of various local emergency response services, such as police, fire units, etc. Contingency arrangements and safe handling and decontamination procedures should be discussed in detail beforehand with emergency response personnel.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- It is important to review and follow guidance in the local area Safety Data Sheet (SDS) also (24-hour emergency telephone numbers are provided in the SDS). In the event of a large spill (such as an overturned tank truck or tank car, ruptured storage tank, etc.) or a moderately large spill, alert local emergency response service units. In the U.S. you can call Dow's Distribution and Emergency Response Center in Freeport, Texas, at 1-979-238-2112, or CHEMTREC for transportation spills at 1-800-424-9300. For Europe, ISOPA provides emergency contact numbers for different EU countries and focal points in many cases. Call any of these numbers at any time – day or night – for advice and/or assistance in containing or cleaning up spills and leaks of any size
- All persons not properly equipped with protective clothing and air-supplied respirators should immediately leave the site of the spill and remain upwind. Only properly trained and equipped personnel should attempt to isolate or contain the spill.
- Dike and contain the spill.
- If possible, trained personnel should prevent further leakage or spread of the leaked material by plugging ruptures or other openings in containers and by diking the spilled material with sand, absorbent clays, etc. Special efforts should be made to prevent the spilled material from entering waterways or drains, including lakes, rivers, streams, sewers, etc. If spilled material does enter waterways or drains, notify local authorities immediately and comply with local regulations.
- If there are standing pools of MDI, the liquid may be pumped (using a drum pump or similar equipment) into closed-top but not sealed containers for disposal (see "Disposal," page 25). Any equipment and containers used must be clean and dry. Properly decontaminate all equipment after use. Do not place the containers in a confined area.
- Cover the remaining isocyanate with plenty of inert absorbent material such as vermiculite (an all-purpose commercial oil absorbent), clay, sand or dirt may also be used. The absorbent should be applied dry. Shovel the MDI/ absorbent mixture into open-top containers. Fill the containers only half full.
- Shovel the reacted residue into open-top containers and remove them to a safe location for further decontamination and disposal, as described on page 25.
- Final decontamination may be accomplished by spraying the spill site with large quantities of water. Use sufficient water to prevent blockage of drains, bilges, etc.
- When cleanup and decontamination have been completed, the area should be carefully inspected by properly trained and equipped personnel. If the area is declared safe, all decontamination equipment may be removed and personnel may be allowed to re-enter.

Solidified Spills

One or more of several methods may be used to remove solidified MDI, depending upon the surface on which the material has been spilled.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- If any of the leaked or spilled material is still in liquid or absorbable form, cover it immediately with plenty of inert absorbent material, such as vermiculite, dirt, sand or clay. Avoid materials such as cement powder.
- Shovel the absorbent/isocyanate mixture into an open-top drum. Cover the drum to prevent spills of the absorbent, but do not make the top pressure tight – it is very important to allow venting of any generated CO₂. Remove the drums to a safe site, away from the operating area, for neutralization. See page 20 for general procedures.

For the part of the spill or leak that is no longer liquid or absorbable:

- Depending upon the surface on which the material has been spilled, workers may use one of the decontamination solutions described on page 21 and a broom to remove films or traces of MDI on surfaces as described below. Workers involved in this operation must be properly equipped with appropriate safety equipment (including chemical goggles and respirators, possibly an air-supplied respirator) and protective clothing (including waterproof coveralls, boots and gloves). After use, carefully wrap the broom in plastic to contain the isocyanate. Dispose of the wrapped broom properly (one method is incineration). In disposal of any wastes, be sure all applicable regulations are met.
- On roadways and other surfaces where damage must be kept to a minimum, solidified MDI may be removed by sandblasting. If sandblasting is used, the contaminated sand must be carefully collected, placed in open-top containers and removed for subsequent decontamination and disposal. Also, workers must be properly equipped with appropriate safety equipment (including chemical goggles and either a self-contained breathing apparatus or, preferably, an air-supplied respirator) and protective clothing (including coveralls, boots and gloves). Selection of specific items will depend on the operation.
- Completely cover the spilled material with the decontamination solution. Allow the solution to remain in place for at least an hour, and then cover the spill with enough absorbent material to soak up all the liquid. Shovel this material into open-top containers, and then remove to a safe, well-ventilated area for decontamination and disposal.
- Wash the contaminated area with large amounts of a decontamination solution. If indoors, thoroughly ventilate the decontaminated area to remove all traces of vapor.
- When cleanup and decontamination have been completed, the area should be carefully inspected by properly trained and equipped personnel. When safe working conditions have been re-established, remove and decontaminate or dispose of protective equipment and return to normal operation.

Disposal

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- Only thoroughly trained and properly equipped persons should participate in disposal operations.
- Keep waste isocyanate widely separated from any other waste such as polyols, catalysts, amines etc.
- Be certain that all disposal procedures are conducted in strict compliance with all applicable country, state and local regulations and ordinances. Liquids are usually incinerated in a proper facility; solids are usually incinerated or landfilled. Refer to current SDS for disposal guidelines.

Drums

Pressurized Drums

In the event that a pressurized drum (e.g., those misshapen due to the presence of carbon dioxide gas) is observed, a potentially dangerous situation exists due to the potential of rupture creating a projectile. **Do not attempt to move the drum.** The area near the drum should be evacuated of all personnel and the drum should be monitored, from a safe distance for a potential rupture.

Taking action like covering with a tarpaulin and puncturing may ultimately be appropriate, but only when adequately trained personnel and suitable protective equipment are available, and when such actions are approved by trained emergency response personnel assessing the situation.

Contact Dow's Distribution and Emergency Response Center in Freeport Texas, at 1-979-238-2112, or CHEMTREC for transportation emergencies at 1-800-424-9300. Call any of these numbers at any time – day or night – for advice and/or assistance in safely mitigating the situation. For emergency situations in Europe, the ISOPA website provides useful information such as emergency response numbers and focal points for countries. For other global regions, please refer to emergency numbers provided in local, jurisdictional safety data sheet.

Decontamination and Disposal

Only properly trained and equipped persons should participate in decontamination and disposal operations.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

MDI products remaining after thoroughly emptying drums may be neutralized by the following procedures:

- Remove emptied drums from the work area to a well-ventilated location or outdoors.
- Remove all bungs. Verify that the drums are empty and once you have confirmed that the drums are empty, and then fill drums with water. Wear protective equipment and keep face away from bung-holes while filling. DO NOT REINSTALL BUNGS.
- Allow drums to stand undisturbed for 48 hours.
- All drums should be scrapped or sent to a drum recycler. They should be drained, triple-rinsed with water, and holed or crushed to prevent reuse. Dispose of drums in an approved landfill or by other procedures approved by applicable authorities.
- Dispose of the drain and rinse fluid according to all federal, state and local regulations, typically in an approved wastewater treatment facility.

Stationary Containers

Cleaning and Decontamination

Occasionally, a stationary container (e.g., a storage or holding tank) used to store MDI will need to be cleaned; however, it is not recommended that the container be washed between each delivery of these products. Before any repair work is initiated, the container should be emptied and thoroughly decontaminated. This can be safely accomplished by adhering to the guidelines that follow.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products.

- Since there are potential hazards associated with MDI during the cleaning and decontamination process, only properly trained and equipped persons should participate in cleaning, decontamination, repair and disposal operations.
- If the container is merely switching service to another MDI product, appropriate plant personnel must inspect it at this point to decide if it is “clean” enough to prevent contamination of the new product. Further cleaning procedures are the responsibility of on-site personnel. The tank must also be dried (i.e., with dry nitrogen to a -40°C [-40°F] dew point) before other products are introduced. After approval by appropriate plant personnel, the tank is ready to receive other MDI products.
- Empty the container. If MDI products are to be transferred to another stationary container, be sure the new container is leak free and blanketed with a dry gas pad (see “Moisture Control,” page 13). Also, monitor the new container to be certain that atmospheric moisture does not cause over-pressurization.
- Remove, clean and properly store all lines, hoses and other connections.

- Open all vents and other openings to allow vapors to escape. If the container is located indoors, be sure the indoor area is also well ventilated (open all doors, windows and vents).
- Provide for the collection of wash and rinse fluids so that they can be disposed of properly, in accordance with federal, state and local regulations.
- To begin cleaning, spray the interior of the stationary container with an appropriate solvent. Then drain the solvent and dispose of properly.
- If the container needs to be repaired or is to be released for other service, it must be thoroughly decontaminated by washing with water to convert any remaining MDI to solid urea. This can be accomplished either by re-circulating water through the tank until all remaining MDI has been converted to solids, or by filling the tank with water and letting it stand undisturbed for 48 hours. It is important, in both cases, that all the tank's vents be open to allow escape of carbon dioxide formed during the decontamination reaction.
- When the remaining MDI has been fully converted to urea, drain the tank completely. Dispose of all used fluids in accordance with all applicable regulations.
- The decontamination procedure will be completed when the remaining solids are removed. Since all tanks are different in some way, the decisions regarding removal of the residue must be made by on-site personnel. Consultation with Dow and/or the tank manufacturer may be helpful. In general, carbon steel tanks usually need to be sandblasted or water-blasted to complete removal of the MDI residue. Stainless steel tanks will need to be buffed to complete this removal of solids. Lined tanks will need at least handbuffing, and often the liners will need to be removed and replaced to complete removal of the MDI residue.
- Once the tank is judged by competent plant personnel to be completely decontaminated, the tank is ready to be repaired or used as storage for other chemicals.

CAUTION: Never weld any metal until it is completely clean and free of all traces of any chemicals.

CAUTION: Personnel entering a tank or other large container should be properly trained, should be monitored by persons outside the tank/container, and should be properly equipped with protective clothing, appropriate eye protection and respiratory protection. Under no circumstances should personnel enter any "empty" storage tank or vessel until all safe tank entry procedures have been completed. Be sure your practices follow any federal, state and local agency regulations. For general guidelines, refer to "Safety Requirements for Working in Tanks and Other Confined Spaces," American National Standard, ANSI-Z117.1-1995 (or latest edition). (In Canada, this issue is regulated under the Canadian Labour Code at the federal level and under the provincial Occupational Health and Safety Acts and regulations.)

The use of solvents may present additional risks of flammability and toxicity. Therefore, such materials should be applied in strict accordance with manufacturer recommendations for safe handling and use.

Health Effects and First Aid

The product Safety Data Sheet (SDS) provides a detailed summary of the health effects of MDI products. Please refer to the applicable product's SDS before using or handling. It is important to refer to a current, local jurisdictional product safety data sheet for detailed guidance and latest recommendations – the appropriate jurisdictional safety data sheet can provide key information such as Risk and Safety phrases required in the EU.

Hazard and Exposure Guidelines

The potential hazard of a given material is based on the degree of toxicity, the individual susceptibility of the user and the likelihood and level of exposure. Responsible users of chemical and industrial materials, therefore, must be concerned not only with the inherent toxicity of such materials, but also with the potential for exposure that may be encountered under specific use conditions. The greater the toxicity, the greater the control required over the level of exposure. Toxic effects can occur not only from a single exposure (acute toxicity), but also from repeated exposures over a period of several hours or days (subacute toxicity), or even from continuous or intermittent exposure over long periods of time (chronic toxicity).

Significant hazards are associated with inhalation of MDI vapors and mists. Thus, exposure limits have been established regarding allowable airborne concentration for MDI in the work environment.

Two values are commonly used to describe those limits: the "ceiling concentration," which is the maximum concentration not to be exceeded, even for a short period of time, and the time-weighted average (TWA), which is the concentration to which nearly all workers may be repeatedly exposed for 8 hours a day, 40 hours a week, without adverse effect. While these values represent the best current thinking of toxicologists and industrial hygienists, they offer no guarantee of absolute safety. Someone who is sensitized to MDI may have an adverse effect with exposure below these guidelines. It is imperative that personnel working with polyurethane chemicals fully understand the hazards associated with their use and are familiar with procedures that will minimize the hazards involved.

The threshold limit value (TLV) for MDI is 0.005 ppm (parts per million) or 5 ppb (parts per billion), expressed as a TWA. This is a value from the ACGIH (American Conference of Governmental Industrial Hygienists) and is not a mandatory guideline. It represents a concentration of airborne material to which most people can be exposed day after day without adverse effects. Refer to your local jurisdictional product SDS for relevant occupational exposure guidelines.

Based on the nature of the health effects caused by MDI, a ceiling value (one which limits even brief exposures to higher concentrations) is believed to be more protective and appropriate. The OSHA permissible exposure limit (PEL) – a 20 ppb ceiling – is the standard for compliance in the United States.

OSHA has not established an 8-hour TWA value. However, the National Institute for Occupational Safety and Health (NIOSH) and the ACGIH have recommended an 8-hour TWA for MDI of 0.005 ppm (equivalent to 0.051 mg/m³). Because federal or state regulations may change, it is essential that users of MDI keep themselves fully informed on the most current regulations and exposure guidelines. Refer to your local jurisdictional product SDS for relevant occupational exposure guidelines.

Handling and Precautions Summary

MDI and other toxic vapor levels in the work environment are best controlled by properly designed equipment and adequate ventilation and exhaust. Combined with safe work procedures, properly designed equipment in good working order can maintain vapor levels within acceptable limits.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products. In addition, refer to a current, local jurisdictional safety data sheet for detailed recommendations.

- All employees must be instructed and periodically retrained in the use of protective and emergency equipment, as well as in preventive procedures. Employees working in areas where contact with MDI is possible should be thoroughly trained in appropriate emergency procedures. Prompt administration of emergency aid can minimize the possible adverse effects of accidental exposure. Medical attention from qualified personnel should be provided as soon as possible.
- Be sure work areas are adequately ventilated to control vapors below employee exposure limits established by Occupational Health and Safety Administration (OSHA) in the United States or Workplace Hazardous Materials Information System (WHMIS) in Canada. Refer to your local jurisdictional product SDS for relevant occupational exposure guidelines
- Regularly inspect and repair exhaust and ventilation equipment. Work area atmospheres should be tested periodically by trained industrial hygienists to be sure that airborne MDI is being controlled at acceptable levels.

NOTE: Available information indicates that the lowest detectable odor level of MDI is approximately 0.4 ppm. Because this odor threshold is significantly higher than the OSHA PEL, odor cannot be relied on to warn of hazardous airborne concentrations of MDI. Vapor levels must be monitored using equipment specifically designed to measure airborne MDI levels.

- For engineering controls, personal protective equipment and first aid, see recommendations in current, local jurisdictional safety data sheet.

- Employment in an isocyanate area may present a health risk to individuals with a history of respiratory problems or allergies. Candidates for employment where occupational exposure to isocyanate may occur should be examined for pulmonary function with particular emphasis on allergic history including asthma or other diseases that may impact lung function.

CAUTION: Exposure to heated MDI can be extremely hazardous, not only because high vapor concentrations are formed, but also because condensation may form airborne droplets. If the product is heated or there is a potential for aerosol formation (e.g. spray applications, inadvertent aerosol release), then, airborne concentrations sufficient to cause irritation of the eyes, upper respiratory tract and lungs may be encountered upon single exposure. **An air-supplied respirator must be worn whenever there is any possibility of exposure to unknown concentrations of airborne isocyanates.**

Health Hazards, Preventive Measures and First Aid

As previously discussed, the product Safety Data Sheet (SDS) provides a detailed summary of the health effects of MDI products. Please refer to the applicable product's SDS before using or handling. It is important to refer to a current, local jurisdictional product safety data sheet for detailed guidance and latest recommendations – the appropriate jurisdictional safety data sheet can provide key information such as Risk and Safety phrases required in the EU.

Inhalation

Health Hazards and Preventive Measures

At room temperature, MDI vapors are minimal due to low volatility. However, certain operations may generate vapor or mist concentrations sufficient to cause respiratory irritation and other adverse effects. Such operations include those in which the material is heated, sprayed or otherwise mechanically dispersed such as drumming, venting or pumping. Excessive exposure may cause irritation to upper respiratory tract (nose and throat) and lungs, and pulmonary edema (fluid in the lungs). Exposure effects may be delayed. Decreased lung function has been associated with overexposure to isocyanates.

MDI may cause an allergic respiratory response. MDI concentrations below the exposure guidelines may cause allergic respiratory reactions in individuals already sensitized. Asthma-like symptoms may include coughing, difficult breathing and a feeling of tightness in the chest. Occasionally, breathing difficulties may be life threatening.

Atmospheric levels should be maintained below the exposure guideline. When atmospheric levels may exceed the exposure guideline, use an approved air-purifying respirator equipped with an organic vapor sorbent and a particle filter. For situations where the atmospheric levels may exceed the level for which an air-purifying respirator is effective, use a positive-pressure air-supplying respirator (air line or self-contained breathing apparatus). For emergency response or for situations where the atmospheric level is

unknown, use an approved positive-pressure self-contained breathing apparatus or positive-pressure air line with auxiliary self-contained air supply. The following should be effective types of air-purifying respirators: Organic vapor cartridge with a particulate pre-filter.

First Aid/Medical Treatment

Move person to fresh air. If not breathing, give artificial respiration; if by mouth-to-mouth, use rescuer protection (pocket mask, etc.). If breathing is difficult, oxygen should be administered by qualified personnel. Call a physician or transport to a medical facility.

Skin Contact

Health Hazards and Preventive Measures

Prolonged contact may cause slight skin irritation with local redness. Staining of skin is possible. Prolonged skin contact is unlikely to result in absorption of harmful amounts. Skin contact may cause an allergic skin reaction. Animal studies have shown that skin contact with isocyanates may play a role in respiratory sensitization.

To handle products, use protective clothing chemically resistant to this material. Selection of specific items such as face shield, boots, apron or full body suit will depend on the task. Remove contaminated clothing immediately, wash skin area with soap and water, and launder clothing before reuse or dispose of properly. Items that cannot be decontaminated, such as shoes, belts and watchbands, should be removed and disposed of properly. Examples of preferred glove barrier materials include: butyl rubber, polyethylene, chlorinated polyethylene and ethyl vinyl alcohol laminate (EVAL). Examples of acceptable glove barrier materials include: Viton[®], Neoprene, Polyvinyl chloride (PVC or vinyl) or nitrile/butadiene rubber (nitrile or NBR).

NOTICE: The selection of a specific glove for a particular application and duration of use in a workplace should also take into account all relevant workplace factors such as, but not limited to: Other chemicals that may be handled, physical requirements (cut/puncture protection, dexterity, thermal protection), potential body reactions to glove materials, as well as the instructions/specifications provided by the glove supplier.

Note that nitrile gloves are acceptable for situations where only incidental contact is anticipated³. Dispose of nitrile gloves after short periods of use (2 hours). For prolonged contact with MDI, wear butyl rubber or

³ Robert, William R., Joe Jadlocki, Vicki Filimeni, "Protecting Workers from PMDI-Solvent Combinations, What Gloves Work Best? Part Two," Polyurethanes Conference Proceedings, October 8-11, 2000. Another good industry reference that provides guidance on suitable glove types is available via the Center for the Polyurethanes Industry Association.

ethyl vinyl alcohol laminated gloves. These gloves also have a limited period during which they provide adequate protection and may need to be replaced often during heavy use.

First Aid/Medical Treatment

Remove material from skin immediately by washing with soap and plenty of water. Remove contaminated clothing and shoes while washing. Seek medical attention if irritation persists. Wash clothing before reuse. An MDI skin decontamination study demonstrated that cleaning very soon after exposure is important, and that a polyglycol-based skin cleanser or corn oil may be more effective than soap and water. Discard items that cannot be decontaminated, including leather articles such as shoes, belts and watchbands. A safety shower should be located in the immediate work area.

Eye Contact

Health Hazards and Preventive Measures

MDI products may cause moderate eye irritation and slight temporary corneal injury. Appropriate eye protection (chemical goggles) should be worn whenever MDI is used and an eye wash fountain should be present in the immediate work area.

First Aid/Medical Treatment

Immediately flush eyes with water; remove contact lenses, if present, after the first 5 minutes, then continue flushing eyes for at least 15 minutes. Obtain medical attention without delay, preferably from an ophthalmologist.

Ingestion (Oral Toxicity)

Health Hazards and Preventive Measures

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

Good industrial practice suggests that contact with the mouth should be avoided. Food should not be prepared or consumed, nor smoking permitted, where MDI is used. Wash hands before smoking or eating³.

First Aid/Medical Treatment

If MDI products are swallowed, seek medical attention. Do not induce vomiting unless directed to do so by medical personnel.

³ Robert, William R., Joe Jadlocki, Vicki Filimeni, "Protecting Workers from PMDI-Solvent Combinations, What Gloves Work Best? Part Two," Polyurethanes Conference Proceedings, October 8-11, 2000. Another good industry reference that provides guidance on suitable glove types is available via the Center for the Polyurethanes Industry Association.

Effects From Repeated Exposure

Tissue injury in the upper respiratory tract and lungs has been observed in laboratory animals after repeated excessive exposures to MDI/polymeric MDI aerosols. Lung tumors have been observed in laboratory animals exposed to respirable aerosol droplets of MDI/polymeric MDI (6 mg/m³) for their lifetime. Tumors occurred concurrently with respiratory irritation and lung injury. Current exposure guidelines are expected to protect against these effects reported for MDI. In laboratory animals, MDI/polymeric MDI did not cause birth defects; other fetal effects occurred only at high doses that were toxic to the mother. Genetic toxicity data on MDI are inconclusive. MDI was weakly positive in some in vitro studies; other in vitro studies were negative. Animal mutagenicity studies were predominately negative.

It is important to review the relevant occupational exposure guidelines provided in your latest local safety data sheet.

Diphenylmethane diisocyanate, the principal active ingredient in MDI products, is a highly reactive and potentially hazardous material, which can adversely affect or injure the eyes, the skin and the respiratory tract, depending on the avenue and the extent of exposure.

While these guidelines represent current thinking and are believed to be conservative, they offer no guarantee of absolute safety. It is imperative that personnel working with MDI fully understand the hazards and are kept fully informed of current guidelines and regulations. Refer to the latest, local jurisdictional SDS for current and specific product information. To obtain SDSs for MDI products made by Dow, call the Dow Customer Information Group (CIG) at the relevant number (Page 52).

NOTICE: The information and recommendations that follow are presented in good faith. However, since this information and the recommendations are provided without charge, and since use conditions are not within Dow's control, Dow does not guarantee any results from the use of the information or the recommendations; no warranty, express or implied, is given. It is the Customer's responsibility to determine that its workplace and practices comply with law and applicable safety standards.

Part 2 – Shipment, Handling and Storage

Drums

MDI-based products are shipped in non-returnable, steel drums.

Carefully review and understand the following safety recommendations and precautions before handling, storing or disposing of MDI products:

1. Before attempting to use the following procedures, operators should be thoroughly familiar with the potential hazards associated with handling and storing MDI.
2. Closely examine each shipment for damaged drums. Drums should be handled and unloaded carefully to prevent damage. Safe methods of unloading trucks include using forklifts very carefully. If damaged drums are found, they should be closely inspected for leaks or punctures. Breached drums should be removed to a dry, well-ventilated area and the contents transferred to other suitable containers. The empty drums should be decontaminated (see page 25). Dispose of drums in accordance with all applicable regulations.

Re-melting Drums of Pure MDI

1. Drums of pure MDI are shipped in temperature-protected trucks as “frozen” or “fused” material. Thus, drums will have to be heated and the product melted before the material can be unloaded and transferred to a reactor or storage tank.

If drum shipments of polymeric or modified MDI products arrive in a crystallized, frozen or fused state, they should be promptly unloaded safely and heated as soon as possible. Polymeric MDI products that have been frozen will exhibit the same dimerization characteristics as pure MDI. Unless proper action is taken to heat or melt the product, dimerization will proceed rapidly and deteriorate both the clarity and assay of the product.

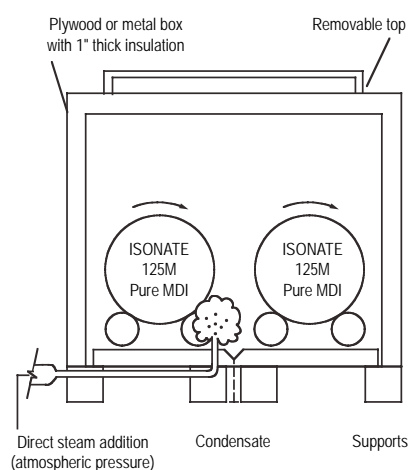
While several methods for melting frozen or crystallized MDI have been developed, the method of choice should be one in which dimer formation is minimized. This can best be accomplished by rapid, even heating of the drums, as follows.

2. The preferred method for heating drums is “drum rolling” (usually at 5 to 10 rpm on a mechanical drum roller) in atmospheric steam (See Figure 5). The principal advantage of this method is that it permits efficient heat transfer – that is, the still-frozen block of MDI cools the liquefied material so that the contents are not heated much beyond 65°C (149°F), the point at which dimer formation can increase significantly. Experience has shown that a frozen drum of pure MDI and modified MDI, with a temperature between 0°C and -20°C (32°F and -4°F) (0°C and -18°C [32°F and 0°F] for polymeric MDI) will usually melt completely (i.e., reach 65°C [149°F]) in approximately 4-10 hours. Also, while 65°C (149°F) is significantly higher than the recommended storage and handling temperatures, it is

necessary to reach this temperature, at least briefly, in order to melt the product both quickly and thoroughly.

CAUTION: The “drum rolling” procedure should be carefully monitored to prevent bumping, rubbing or other conditions that could puncture or otherwise damage the drums. Use of water baths to melt drums of frozen MDI is not recommended as it has a higher potential for product contact with water – this can lead to CO₂ generation and over-pressurization which can lead to drum explosion. Refer to all precautions provided in the local, jurisdictional SDS prior to implementing the melting process.

Figure 5: Melting MDI by Drum Rolling in Direct Steam⁴



3. Other methods for heating drums, which may result in less satisfactory product quality, are “static melting” in a “steam chest” and drum rolling in hot air; however, these methods can be recommended as temporary measures only, to be used only until appropriate equipment becomes available. The important criteria (needed to minimize dimerization and to protect product quality) in any drum-heating method are agitation and quick but even heating – criteria that can best be met by drum rolling in atmospheric steam. Dow does not recommend static melting with an electric heating apparatus. Also, drums that have been opened should be re-blanketed with a dry gas pad (see “Moisture Control,” page 13) before heating. All drums, whether previously opened or not, should have their bungs tightened securely.
4. When steam is used, the heat – after three to five hours of heating – will usually evaporate any free moisture remaining on the drum heads. Nevertheless, after heating, drum tops should be carefully wiped dry with a dry cloth. Also, the dust cap should be removed carefully. Then, the 2-inch bung should be carefully loosened slightly to relieve any buildup of internal pressure. After the melting process has been completed, the drums should be removed from the heating equipment and, if not used immediately, placed in a retaining oven set at recommended storage temperature (refer to Tables 2 and 3).

⁴ This drawing is for illustrative purposes only. Dow does not assume responsibility for actual design. See notice on the back cover of this brochure.

CAUTION: If pure MDI has been exposed to significant atmospheric moisture, irreversible changes will occur and restoring the product to its original assay will be impossible. Thus, any drum suspected of being moisture-contaminated should not be heated.

5. Examine the product for clarity while it is still liquid. Should unexpected storage or melting conditions result in turbidity after the product has returned to room temperature, it can usually be re-clarified by gentle heating; however, to prevent further increases in precipitation of dimer, the product should be used as soon as possible. Exercise extreme care when opening the heated drum.
6. Ideally, drums should be unloaded or emptied via a totally enclosed system (i.e., dip-tube technique or equivalent) in which both the drum and storage tank are blanketed with a dry inert gas pad. However, drums may also be unloaded with conventional steel or stainless steel drum pumps or with air-driven or hand-operated pumps or ball valves mounted on the 2-inch bung.
7. Install the proper fittings to transfer the product to the reactor, closed holding tank or weigh tank. Only stainless steel fittings should be used. To maintain product quality, do not use copper, aluminum or galvanized steel. Also, discharge to the reactor or tank should be through continuous piping that has been insulated and traced where necessary to maintain recommended storage temperature (See Tables 2 and 3).
8. To prevent moisture contamination during unloading, the 3/4-inch vent should be equipped with a dry purge gas breather or drying tube. This device will also prevent the collapse of the drum during unloading. Also, a purge gas “flush line” should be installed to force any remaining MDI through the filter and lines and into the tractor or tank.

CAUTION: NEVER PRESSURIZE DRUMS

9. To remove the small amount of “solids” that can sometimes form during shipment and storage (usually because of inadequate temperature control or product contamination), it may be necessary to pass the product through an in-line filter, with tempered-water temperature control, during transfer from the drum to the reactor.

Recommended filters for this purpose include filters such as Cuno filters with polypropylene cartridges, Velcon filters containing fiberglass or phenolic-impregnated filter material with a 25-micron retention, or a 25-micron sock polypropylene filter.

It should be emphasized again that solids can be caused either by exposure of the product to improper temperatures or by product contamination. The key to minimizing dimerization is proper temperature control. Protection of the product from exposure to various contaminants – principally water – will prevent the formation of solid ureas. Water contamination can also cause the buildup of excessive pressure in a closed drum due to the evolution of carbon dioxide.

10. After unloading, disassemble all portable or temporary transfer lines. Clean them with an appropriate solvent⁵, then rinse, dry, tightly cap and store them in a dry location until next use. When not in use, pumps and valves should be protected from atmospheric moisture by tightly capping or plugging all open ends.

Permanent transfer lines should always be left filled with product and flushed only for maintenance using a dry purge gas and then re-capped. It should be ensured that the temperature of the line is appropriate for product type and quality. See also “Moisture Control” page 13.

Totes

Totes contain large volumes of modified or polymeric MDI product. For proper handling of totes, please refer to the “Drums” section on page 34. Re-melting will not be required for totes because they contain only liquid products. If storage in the customer’s location results in solidification of tote contents, customer is responsible for disposing of tote in accordance with all applicable regulations.

NOTICE: The information and recommendations that follow are presented in good faith. However, since this information and the recommendations are provided without charge, and since use conditions are not within Dow’s control, Dow does not guarantee any results from the use of the information or the recommendations; no warranty, express or implied, is given. It is the Customer’s responsibility to determine that its workplace and practices comply with law and applicable safety standards.

Storage

Wide fluctuations in temperature, in either the solid or molten state, will invariably result in exceedingly high levels of dimer formation. Thus, the key to minimizing dimerization is proper temperature control.

To keep storage temperatures from fluctuating, the storage room should be equipped for “quick recovery” after being opened. Although MDI-based products will slowly dimerize with time, low levels of dimer (i.e., 0.6 percent to 0.8 percent) may not ordinarily affect product appearance or performance. Dimer formation above this level can cause the product to become cloudy (dimer will precipitate out to insoluble deposit) – certain elastomeric products derived from this material may be adversely affected.

NOTE: Product that has been exposed to temperatures outside the recommended ranges should be checked for quality before use.

The two principal conditions that favor “polymer growth” or the formation of solids, or that can otherwise affect the quality of MDI products in storage are:

⁵ The use of cleaning solvents may introduce additional hazards of toxicity or flammability. Such materials must be used in strict compliance with manufacturer recommendations and precautions.

1. Exposure of the product to water (including water vapor) and/or oxygen
2. Exposure of the product to temperatures outside of the range of recommended temperatures (see Tables 2 and 3):

For pure MDI, more details are listed in Table 4 and Figure 6 for rates of dimer formation vs. temperature. In addition, see data on “storage life,” which may be loosely defined as the period of time during which the product may still be melted to form a clear liquid.

Consult your Dow representative for further information or specific needs on temperature control.

NOTE: Pure MDI must be stored as a liquid at 41 - 45°C (106-113 °F) or as a solid at -18°C (0°F) or below!

Drum Storage

In the unlikely case that modified/polymeric MDI drum shipments arrive frozen or crystallized (depending on ambient temperatures, shipping delays, etc.), to protect product quality and to minimize dimer formation, frozen drums should be unloaded promptly and transferred to a properly equipped heating or melting facility (see “Drums,” page 34 for specific instructions on pure MDI). Later, when the original solution has been reformed, the drums should either be placed in a heated storeroom or emptied and the contents transferred to a reactor or heated storage tank. If the product is not to be used either immediately or shortly after heating, the drums should be kept at appropriate storage temperature. (Consult your Dow representative for further information or specific needs on temperature control). The drums should be stored on pallets to allow the warm air to circulate under and around them.

Segregate drums of MDI such that they are not stored along with other drums containing incompatible materials described in earlier sections. Finally, drums should be stored in such a way as to minimize the possibility of accidental damage and product contamination – especially by water. This may be accomplished by handling the drums with care and by stacking them on their sides. This will not only help protect the drums from external damage, but will prevent water from collecting on the drum tops. Before drums are stored, they should be carefully examined for damage. If damaged drums are found, they should be closely inspected for punctures or leaks. Breached drums should be removed to a dry, well-ventilated area and examined. Contact Dow concerning drums containing solid material. Do not store outside, protect from rain and temperature variations.

Drum Storage for Pure MDI

Drum shipments of pure MDI will arrive “cold” – that is, in a frozen or crystallized state, usually at temperatures below -18°C/0°F or at least below 0°C/32°F (maximum). To protect product quality and to minimize dimer formation, frozen drums should be stored immediately upon arrival in a refrigerated storeroom equipped to maintain a uniform temperature - see recommended temperatures in Tables 2 and 3. Although the rate of dimer formation is lowest when the product is in a solid state and temperatures are

kept as low as possible, storage temperatures as high as 0°C (32°F) may also be used if higher levels of dimer are acceptable in processing. For information on “Re-melting Drums of Pure MDI,” see page 34.

In the molten state, dimer formation is lowest at 43°C (110°F); that is, slightly above the melting point of 38°C (100°F). Thus, heated drums should be emptied promptly and the contents transferred to a reactor or heated storage tank. If the product is not to be used either immediately or shortly after heating, maintain at recommended temperature for liquid pure MDI – see Tables 2 and 3. Adjust formulation and blend so that all the MDI is completely consumed in the blend/formulation; Recommendation is to not keep molten drums for more than 48 hours. Never re-freeze melted pure MDI.

CAUTION: Virtually all chemicals possess some degree of toxicity. Before handling a new chemical, it is essential that its toxicological properties, as well as any potential hazards associated with its handling and use, be thoroughly studied and understood. Based on this information, appropriate health and safety standards and procedures should be established and maintained.

Obtain a copy of the current SDS for the appropriate MDI product. Copies are available upon request from Dow's Customer Information Group by calling the relevant number provided on page 52.

Isocyanate

To maintain product quality, MDI liquid or vapor should not be exposed to equipment containing copper, aluminum, zinc, tin or their alloys, including brass, bronze or galvanized materials. Also, do not expose MDI liquid or vapor to either rubber or synthetics, except Teflon fluorocarbon or Viton fluoroelastomer.

Silica gel charges

Silica gel charges associated with the tanks must be removed and the system thoroughly cleaned, dried and purged with a dry, inert gas pad prior to use.

Tote Storage

Dow ships only liquid, modified and polymeric MDI products in totes. Most modified MDI and polymeric MDI products store well at 24°C to 41°C (75°F to 105°F). Store totes in such a way as to minimize the possibility of accidental damage and product contamination — especially by water. Before totes are stored, they should be carefully examined for damage. If damaged totes are found, they should be closely inspected for punctures or leaks. Damaged totes should be removed to a dry, well-ventilated area and examined. Contact Dow concerning totes containing solid material. Dispose of totes that contain solid or partially solid material in accordance with all applicable regulations.

Bulk Storage Systems

A properly designed and well-constructed bulk storage system for MDI should:

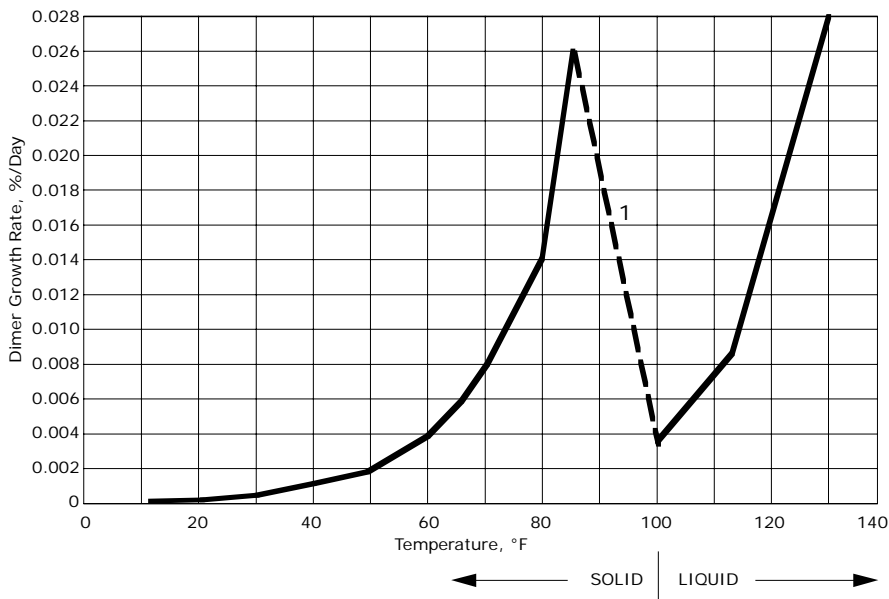
- Contribute to and encourage safe handling — especially in loading and unloading the product.

- Minimize the possibility of tank rupture or leakage at joints, seams, welds, valves and/or other connections.
- Permit safe and easy unloading from tank cars, tank trucks, drums and totes.
- Provide for effective moisture and temperature control.
- Prevent contamination by atmospheric moisture, chemicals, etc.
- Minimize any possibility of fire.

Before attempting to construct such a system, designers should familiarize themselves with the physical, chemical and mechanical properties of the specific MDI-based product and with the various safety recommendations and precautions associated with its handling and storage. A properly designed system must not only include the physical layout of the storage tank and its associated facilities and equipment, but must also include a plan for personnel safety in all areas of the operation. The establishment of safe work procedures must be an integral part of any bulk storage system. In addition, designers should carefully consider all applicable insurance requirements, as well as governmental codes and regulations, and should consult with all appropriate local and state agencies during each stage of planning and construction.

NOTE: The equipment described is typically used in bulk storage systems for MDI-based products. However, these items are merely components of typical systems and must not be considered a finished design. Other equipment, similar to the items listed, may give equally good results.

Figure 6: Dimer Growth¹ of ISONATE 125M Pure MDI as a Function of Temperature²



¹Dimer formation between 86°F and 100°F is so rapid that accurate data are unavailable

²Values will vary with age and use conditions; not to be construed as specifications

Table 4: Approximate Storage Life¹ of ISONATE 125M Pure MDI at Various Storage Temperatures

Temperature °C(°F)	Storage Life (Days) ^{2,3,4}
-17.8 (0)	300
-12.2 (10)	310
4.4 (40)	68
10 (50)	33
25 (77)	See note 5
40.6 (105)	25
43.3 (110)	25
46.1 (115)	23
48.9 (120)	20

¹Values will vary with age and use conditions; not to be construed as specifications.

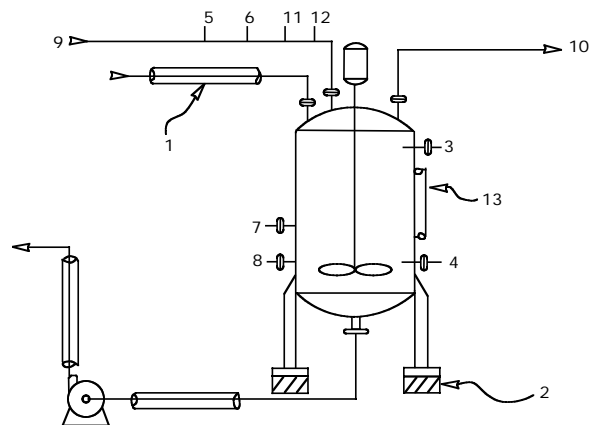
²Storage life is taken as the period of time during which the product can be melted to a clear liquid by melting procedures recommended.

³Storage life includes the average storage time at a Dow plant or warehouse.

⁴Storage life of solid pure MDI is not valid when shipped in non-temperature controlled vans.

⁵Temperature ranges between 10°C (50°F) and 37.8°C (100°F) give the highest dimer growth.

Figure 7: Recommended MDI Storage System¹



MDI Storage Instrumentation

- 1. Piping Temperature Maintenance Control
- 2. Weigh Measurement
- 3. High Level Alarm Switch
- 4. Low Level Alarm Switch
- 5. Pressure Measurement
- 6. Pressure Indication
- 7. Temperature Measurement
- 8. Temperature Indication
- 9. Tank Pressure Makeup
- 10. Tank Pressure Venting
- 11. Tank Over-Pressure Relief
- 12. Tank Vacuum Relief
- 13. Tank Temperature Maintenance Control

¹ This drawing is for illustrative purposes only. Dow does not assume responsibility for actual design. See notice on the back cover of this brochure.

MDI Storage Recommendations

NOTICE: The information and recommendations that follow are presented in good faith. However, since this information and the recommendations are provided without charge, and since use conditions are not within Dow's control, Dow does not guarantee any results from the use of the information or the recommendations; no warranty, express or implied, is given. It is the Customer's responsibility to determine that its workplace and practices comply with all law and applicable safety standards.

NOTE: Copper (including brass), zinc (galvanized) and aluminum must not be used in contact with MDI in equipment, pipe, valves, fittings, instruments or tubing.

Storage Tank

Sized to meet customer needs; however, the minimal capacity of each tank should be equivalent to 150 percent of maximum shipment size.

ASME Sect. VIII pressure vessel designed for minimum rating of -5 to 50 psig at 350°F. Material of construction is carbon steel with epoxy or phenolic-epoxy lining (Chem-Pon 2310 R epoxy lining, Phenguard phenolic-epoxy, Plastite 7122 phenolic-epoxy, or equivalent).

Special design points—top inlet liquid nozzles should be built so as to direct the liquid at the side wall to minimize splashing. Baffles — requires 4 sidewall baffles 1/72 of vessel I.D. off wall and seam to seam if agitator is used. Baffle width equal to 1/12 of vessel I.D.

All nozzles must be heated by jacketing, tubing coil or electric tracing (manway may be exception for jacketing).

Agitation

MDI should be mixed to keep uniform composition and temperature, aid heat transfer and keep any dirt from settling.

1. Top-entering agitator

Advantages: Maximum turnover rate of tank contents, mixing of all parts of the tank, no problems with fouling, operating portion can be repaired without emptying the tank.

Disadvantages: Requires a mechanical seal, more expensive, requires maintenance, tank will require baffles.

2. Eductors

Advantages: Inexpensive (requires incremental extra horsepower in tank pump).

Disadvantages: Can foul (plug or become restricted); difficult to maintain without emptying the tank,

less efficient in mixing total contents of tank, less efficient in keeping solids suspended.

Tank Temperature Maintenance Temperature maintenance system must maintain the MDI-based products at the recommended ranges listed in their respective SDS; tank skin temperature must be such that recommended relevant storage temperatures for the product category are not exceeded.

1. Integral jacket

Advantages: Best heat transfer, no on-site installation, easy to insulate, jacket nozzles positioned at design of vessel.

Disadvantages: Most expensive; if water is used as heat transfer fluid, it can corrode shell or stress crack the vessel shell (and get into process side); difficult to retrofit on an existing tank.

2. Loose pipe coils

Advantages: Heat transfer fluid does not contact shell (no corrosion of shell), about the same cost as panel coils, thicker wall than panel coils, no on-site installation.

Disadvantages: Difficult to repair leaks, requires heat transfer cement, difficult to retrofit on an existing tank.

3. Panel coils

Advantages: Heat transfer fluid does not contact shell (no corrosion of shell), standard designs and sizes available, easy to replace, easy to retrofit on an existing tank.

Disadvantages: Requires heat transfer cement; panels have thin walls; for same area coverage requires more piping, fittings and valves for hookup.

4. Electrical heat pads/tracing

Advantages: Least expensive option to install for either new or existing tanks, easy to insulate, no heat transfer fluid required, easy to replace.

Disadvantages: Control must be carefully designed to avoid hot spots on wall, each section of tape or pad is independent (could overheat).

Insulation

Polyurethane rigid foam - Polyisocyanurate - 2 pounds/cubic foot; indoor tank thickness - 1-1/2-inch (3.8 cm); outdoor tank thickness - 2 inches (5 cm). In addition to insulation, outdoor tanks should be sheltered by an effective weather cover to protect them from rain, snow, ice, etc. Insulation integrity must be maintained to ensure good temperature maintenance.

Pumps

Transfer of MDI by pump is preferred to "pressure" transfers because it eliminates excess venting of the storage tank. Pumps without seals are recommended to avoid seal leaks and possible contamination of MDI by seal fluid. Pumps should be stainless steel construction of wetted parts.

1. Magnetic coupled pump

Advantages: Easier to maintain.

Disadvantages: More expensive than canned pump, greater temperature increase of the MDI case cooling flow.

2. Canned pump

Advantages: Less expensive than magnetic coupled pump, lower temperature increase of the MDI case cooling flow.

Disadvantages: More difficult to maintain.

Pumps should be heated with integral jacketing or by heat tracing. Bearing design should have maximum clearances possible to avoid problems with solids restricting cooling flow in the case. For cases where clearances cannot be adjusted, install a strainer on the external cooling connection from the pump discharge to the pump case. Dow recommends pumps with a bearing wear indicator, vibration monitor and internal case cooling fluid temperature indicator. Pumps must never run dry, suction valves must never be throttled and discharge valves must always remain open when pumps are in operation. Pumps should be operated at all times when there is sufficient liquid for suction in the tank. When the pump is not in service, it must be drained and purged with dry nitrogen.

Filters/Strainers

Stainless steel housing with stainless steel core; for filters, 25-micron polypropylene filter bag. Housing should be designed for 150 psig at 177°C (350°F). Housing must be jacketed or heat traced to maintain optimum temperature. Off-line (spare) unit must be clean and dry. If unit is out of service, it must be drained and purged with dry nitrogen.

Piping, Valves and Fittings

Piping, valves and fittings should be made of stainless steel, jacketed or heat traced to maintain optimum temperature. They must be built with no pockets – preferably to drain dry, but if not possible, drain valves should be positioned at any low points. Jacketing or heat tracing system must maintain temperature of piping, instruments and flanges at 43°C (110°F) +/-5°C or °F. For electrical tracing, pipe skin temperature measurement controls the amount of heating. The jacketing or tracing system must be designed to ensure that the maximum piping skin temperature does not exceed 49°C (120°F). Insulation for piping, valves and fittings - polyurethane rigid foam - polyisocyanurate - 2 pounds/cubic foot; indoor piping thickness - 1-1/2 inches (3.8 cm); outdoor piping thickness - 2 inches (5 cm). Insulation integrity must be maintained to ensure good temperature maintenance. Preferred valves are plug or ball with sleeves or seats made of Teflon and without internal lubrication. Gaskets are flat ring (1/16 inch thick) filled PTFE with granular silica filler (Gylon Style 3510 white, fawn or equivalent). Sample valves should be piston type, Strahman or Fetterrolf Ram.

Instruments

1. Flow meter — Mass flow meter installed with provision to completely drain when not in service (Bailey, Micromotion or equivalent).
2. Level measurement — Shear beam flex-mount, semi-floating weigh cells (Mastron or equivalent). High- and low-level alarm points should be ultrasonic level switches set at 95 percent and 10 percent tank level respectively (Sensall or equivalent).
3. Pressure — Measurement by electronic pressure transmitter with diaphragm capsule type element (Rosemount or equivalent). For pressure indication —diaphragm sealed, bourdon tube pressure gauges.
4. Temperature — Measurement by thermocouple, RTD, or bi-metallic type dial thermometer with 316 stainless steel thermowell.
5. Pressure control — Makeup by pressure regulator on dry nitrogen supply. Venting by globe style, pneumatic control valve with positioner.
6. Over/under pressure relief — Pressure and vacuum safety valves sized by standard practice for worst-case relief requirements.
7. Environmental control — The vent gas from the tank must be passed through an activated carbon-containing vessel or canister before release to the air. Sizing of the carbon-containing vessel or canister must be adequate for maximum expected vent flow (which will be when piping is blown back to the tank).
8. Unloading vapor return — The tank should be equipped with a vapor return line to vent back to the tank truck during unloading.

Bulk Storage Equipment

For pure MDI and prepolymers, construction materials for tanks, lines, pumps, etc., should be Series 300 stainless steel or stainless cladding. Other materials, such as mild steel, epoxy or phenolic-coated metal and GRP tanks, have all reportedly affected product quality and are not recommended — particularly if MDI products of the very highest quality are required.

For polymeric MDI, carbon steel tanks and black iron piping will not affect product quality.

NOTE: Copper (including brass), zinc (galvanized) and aluminum must not be used in contact with MDI in equipment, pipe, valves, fittings, instruments or tubing.

Insulation

Given the relatively high freeze range of the various MDI products, it is strongly recommended that storage tanks be located indoors; however, if storage tanks must be located outdoors where they may be exposed to extremes of temperature, they should be primed and coated with a high quality epoxy paint

and then insulated with either a 1-inch to 1-1/2-inch (2.5 cm to 3.8 cm) minimum thickness of polyurethane rigid foam or a 2-inch thickness of fibrous glass.

If tanks are located indoors where room temperatures are maintained (i.e., 24°C to 29°C [75°F to 85°F]), heating may not be required. Please check the current technical data sheet or SDS for the recommended storage temperature for your MDI-based product. Rooms for interior storage tanks that have been insulated with plastic foam, should be covered with an effective flame barrier (refer to foam manufacturer recommendations) to minimize the possibility of fire.

Relief Valves

Storage tanks containing MDI should be equipped with a top-mounted pressure safety valve (PSV), with relief pressure set at the tank design pressure (15 psig). This is extremely important as it provides over-pressure (i.e., rupture) protection should the normal pressure venting system fail. Because this is a critical valve, it should be cleaned and inspected yearly and every time it is opened.

NOTE: An automatic venting system (AVS), mounted either on the tank top or on the pad gas blanket line, is required. This system should be set for 10 psig. A manual vent valve is recommended. To prevent an accumulation of vapors, indoor tanks must vent or terminate outdoors and out of the way of any personnel.

Gauges

Gauges should be provided at the pump, before and after filters, near the process, and on top of the tank. They should be protected by a sealed diaphragm filled with a non-hydrocarbon fluid. Gauges are also advisable on steam and air lines and on equipment where gases or liquids are handled (i.e., at chillers or heat exchangers).

A temperature gauge should be mounted on the side near the bottom of the tank. The temperature of the product may be accurately monitored with a dial-type thermometer inserted in a suitable thermowell. To achieve greater heat transfer for a more accurate temperature measurement of the contents, be sure the thermometer is in direct contact with the thermowell.

Sample Valves

To facilitate product sampling, a three-way sample valve should be installed on a stainless steel tubing line going from the pump discharge to suction.

Piping

Lines (including transfer lines, piping and fittings) should be made of insulated carbon steel with self-limiting electrical heat tracing. Line sizes should be determined by product flow rate. Do not use galvanized pipe.

Heat Exchangers

If a heat exchanger is used, the MDI should flow inside the tubes, while the heating or cooling medium should be on the shell side of the exchanger. This will facilitate cleaning the tubes, which should be done periodically. The heat exchanger should have sufficient area to achieve the required product outlet temperature, with close approach between the product and shell-side fluid temperatures. Water should not be used as the heating or cooling medium because of its reactivity with isocyanates. A barrier fluid (that has no reactivity with isocyanate) such as DOWTHERM* heat transfer fluid, should be used.

NOTE: The product pressure should always be higher than the pressure of the heating or cooling medium.

Pad Gas

A dry nitrogen blanketing system, tank-top mounted, set for 5 psig¹, and with a maximum water content of 65 ppm (dew point: -40°C [-40°F]), is recommended. (See "Moisture Control," page 13.)

Pressure Control Valves

Use a pressure control valve¹ to relieve the pressure in the MDI storage tank.

Level Indicator

A flange differential pressure transmitter mounted near the bottom on the side of the tank is recommended for level indication. It should be sealed from the isocyanate with a stainless steel diaphragm at least 4 inches (10.2 cm) in diameter to reduce the possibility of plugging. The low side should be connected to the inlet nitrogen pad line downstream of the pressure control make-up valve.

Meters

Use suitably sized meters. Meters should contain no aluminum, brass or copper alloys, or synthetics other than Teflon fluorocarbon or Viton fluoroelastomer.

Valves

Carbon steel plug or ball valves may be used, provided no internal lubrication is required. If valve packing is required, it should be a nongraphited material or material impregnated with Teflon fluorocarbon fiber, or braided Teflon fluorocarbon fiber. Valves should have seals of Teflon.

Gaskets

Non-graphited gaskets impregnated with Teflon fluorocarbon or braided Teflon fluorocarbon fiber may be used. Spiral-wound gaskets made of Teflon fluorocarbon are also suitable.

¹These pressures should be set to conform with the design specifications of the storage vessel.

Hoses

Hoses should be made of either Teflon fluorocarbon or Viton fluoroelastomer. For permanent and continuous service, use only flexible, stainless steel hoses lined with either Teflon fluorocarbon or Viton fluoroelastomer.

Electrical

Explosion-proof wiring and equipment should be used in all areas where flammable vapors or dusts are likely to be present. All electrical equipment should be grounded. Electrical work must conform to all applicable codes and ordinances. When ordering electrically operated equipment, be sure to indicate the type of electrical service available. (See "Fire and Explosion Hazards," page 18.)

Foundations

Depending on load and soil conditions, reinforced concrete pads or pads with reinforced concrete piers may be used. In addition, tank bottoms should be coated and, if outdoors, sealed to the foundation with asphalt.

Paint

As an added precaution, all equipment used outdoors should be carefully cleaned and then coated with a suitable primer and finish coat.

Dual-Service Equipment

Generally, equipment should not be used for more than one type of product. Current sophisticated systems cannot tolerate contamination.

Drains

All equipment should be provided with drains and should be designed to drain completely. Piping should slope toward low points equipped with drains.

Ventilation

Indoor storage systems should be housed in a separate room, equipped with exhaust fans and intakes to minimize vapor accumulation in the event of a leak or spill. Tank areas should be diked to contain 110 percent of the largest tank in the diked area (if possible, unless local ordinances require more) with no open drains within the diked area. Only compatible materials should be located in the same dike. Flammable material should not be contained in the same dike.

Additional Considerations

- Waste control, disposal and air pollution control measures should comply with federal, state and local rules, regulations and orders. Proper systems and operational controls should be instituted and carefully maintained.
- All equipment and facilities, as well as their installation, should conform to the specifications and requirements of appropriate federal, state and local codes and ordinances.
- All equipment and materials should be compatible with the product to be handled and should be installed in strict compliance with manufacturer recommendations.
- All systems should be bonded and grounded. (Bonding and grounding cables should be made available at all loading and unloading stations.)
- All electrical equipment, such as motors, switches, etc., as well as their installation and use, must conform to codes established by Underwriters Laboratories (UL).
- All tanks should be equipped with a low-point drain so that the tank may be completely emptied for cleaning, inspection or repair.
- All liquid bulk storage systems should be hydrostatically tested prior to insulation or use and then thoroughly dried before use.

APPENDIX - Additional Resources

Printed Materials

For further information, you may want to consult literature published by the following firms and organizations: (Note that addresses, telephone numbers and websites provided are to the best of our knowledge and not guaranteed)

American Chemistry Council

1300 Wilson Blvd.

Arlington, VA 22209

(703) 741-5000

www.americanchemistry.com/dii

American Conference of Governmental Industrial Hygienists (ACGIH)

1330 Kemper Meadow Dr., Suite 600

Cincinnati, OH 45240

(513) 742-2020

www.ACGIH.org

American Industrial Hygiene Association (AIHA)

2700 Prosperity Ave., Suite 250

Fairfax, VA 22031-4307

(703) 849-8888

www.AIHA.org

American National Standards Institute (ANSI)

25 West 3rd St., 4th Floor

New York, NY 10036

212-642-4900

www.ansi.org

ASTM International

100 Barr Harbor Dr.

West Conshohocken, PA 19428-2959

(610) 832-9585

www.ASTM.org

Center for the Polyurethanes Industry (CPI)

1300 Wilson Blvd.

Arlington, VA 22209

703-741-5103

www.polyurethane.org

International Isocyanates Institute

<http://www.diisocyanates.org/>

ISOPA - European Diisocyanate and Polyol Producers Association

Av. E. Van Nieuwenhuysse Laan 4, Box 9

B-1160 Brussels

Tel: ++32 2 676 74 75

www.isopa.org

National Institute for Occupational Safety and Health (NIOSH)

4676 Columbia Pkwy

Cincinnati, OH 45226

1-800-35-NIOSH (1-800-356-4674)

www.cdc.gov/niosh/homepage.html

U.S. Department of Labor

Occupational Safety & Health

Administration (OSHA)

Office of Public Affairs – Room N3647

200 Constitution Avenue, NW

Washington, DC 20210

(202) 693-1999

www.osha.gov

Manufacturers and Suppliers of Respiratory Equipment

The authority for approving or certifying respirators is held jointly by the National Institute for Occupational Safety and Health (NIOSH) and the Mine Safety and Health Administration (MSHA). (In Canada, refer to the Canadian Standards Association [CSA] standard "Selection, Care and Use of Respirators," Z94.4.) For current information on the status of approvals of respirators, e-mail NIOSH: pubstaf@cdc.gov, or call 1-800-356-4674. Another source for information is the OSHA Respiratory Protection Standard 29CFR 1910.134.

In the EU, CE Marking on a product is a manufacturer's declaration that the product complies with the essential requirements of the relevant European health, safety and environmental protection legislation – consult current, local language SDS for respirator references.

Product Stewardship

Dow strongly encourages its customers to review both their manufacturing processes and their application of Dow products from the standpoint of human health and environmental quality. To help ensure that Dow products are not used in ways for which they are not intended or tested, Dow personnel will assist customers in dealing with ecological and product safety considerations. Dow product literature, including current Safety Data Sheets must be consulted prior to use of Dow products. Additional safety and handling information can be obtained by contacting Dow's Customer Information Group at:

CIG North America

1-800-441-4DOW (4369)

CIG Europe

+800-3-694-6367 (International toll-free from Austria, Belgium, Denmark, Finland [prefix 990], France, Germany, Hungary, Ireland, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom)

800 783 825 (Italy toll-free national)

0800 99 5078 (South Africa toll-free national)

CIG Pacific

+800 7776 7776 (except Indonesia and Vietnam)

CIG Brazil

+55-11-5188-9222

CIG Latin South Region (Argentina, Chile, Peru)

+54-11-4510-8777

CIG Latin America (General)

+55-11-5188-9000

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