

# TDI Handbook

## North America



 **BASF**

The Chemical Company

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# 1. Introduction

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

## **BASF Commitment to the Polyurethane Industry**

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

- Urethane Chemicals
  - MDI (diphenylmethane diisocyanate)
  - TDI (toluene diisocyanate)
  - Polyols (polyether, polyester)
- Polyurethane Systems
- Polyurethane Elastomers / Thermoplastics
- Microcellular Polyurethanes

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

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



Figure 1. BASF Urethane Chemical Production Sites.

BASF manufactures and markets three of key urethane chemicals - TDI, MDI, and Polyols. TDI is produced by BASF Corporation at Geismar, LA. U.S.A., by BASF Schwarzheide GmbH at Schwarzheide, Germany, by BASF Company Ltd. at Yeosu, Korea and by Shanghai BASF Polyurethane Company in Caojing, China. BASF has established a reputation in the worldwide polyurethane market as a highly reliable source of TDI.

The trademarks for BASF TDI are Lupranate® T80, Lupranat® T80, and SYStanat® TP80. TDI is an important chemical building block in a wide variety of polyurethane applications. Its most important use is in the production of flexible polyurethane foams for furniture, bedding, carpet underlay, and automotive seating. TDI is also used in the production of adhesives, coatings, sealants, and elastomers.

Like many reactive chemicals, “TDI products” can create hazards if handled carelessly. The purpose of this publication is to outline certain precautions, the observance of which will reduce these hazards in handling diisocyanates under normal and emergency situations.

All persons associated with the transportation, storage, or handling of TDI or products containing TDI, must be fully aware with their hazards and trained in the recommended normal and emergency handling procedures.

This publication is intended to provide general guidance only. In some countries, specific regulations supplement or modify the guidance given herein. All users of TDI products must be fully informed on the most current guidelines and the regulations of all applicable authorities. Users of TDI are strongly urged to consult the appropriate regulatory authorities before finalizing specifications for processing, handling, and storage equipment.

The current Material Safety Data Sheet (MSDS) should be used in conjunction with this publication because the MSDS is updated as changes in regulatory requirements occur. Material Safety Data Sheets can be obtained directly from your BASF representative.

## 2. The TDI Products

### TDI Production Process

In the TDI process, toluene diamine (TDA) is manufactured by the catalytic reaction of dinitrotoluene (DNT). TDA is in turn reacted with phosgene (carbonyl chloride) to produce toluene diisocyanate (TDI). Figure 3 gives a view of the production steps to produce TDI.

BASF TDI is an 80:20 mixture of the 2,4- and 2,6-TDI isomers assaying 99.5% TDI minimum. TDI is produced in a number of grades that differ slightly in acidity and hydrolyzable chloride content. Increased acidity of TDI allows broader processing latitude in some applications. Type I is used in flexible slab polyurethane foam and Type II is used primarily in coating, adhesive, sealant, and elastomer (CASE) applications wherever an intermediate prepolymer is produced.

### Properties of TDI

TDI is more dense than water and will sink to the bottom of water-filled containers. Although it reacts exothermically with water, the rate of reaction is very slow at temperatures below 50°C (122°F). At higher temperatures the reaction becomes progressively more vigorous and can be violent. The reaction of TDI with water forms both carbon dioxide (CO<sub>2</sub>) and insoluble polyurea compounds. Even small quantities of water may produce sufficient CO<sub>2</sub> to rupture sealed containers.

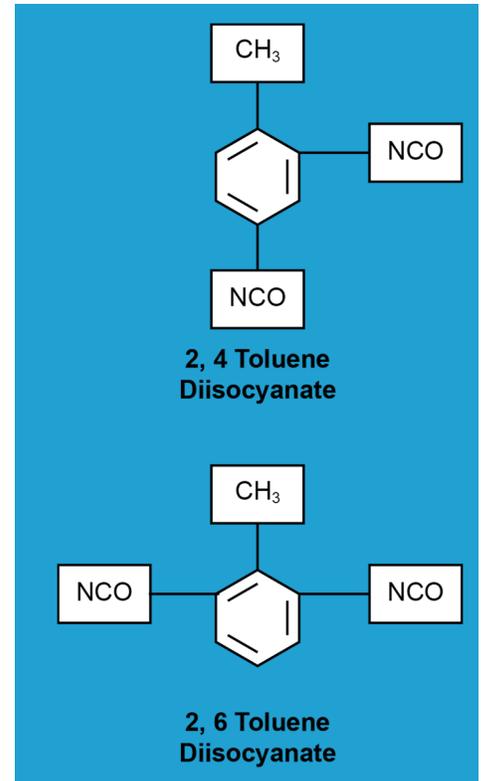


Figure 2. Molecular Structures of 2,4- and 2,6-TDI Isomers

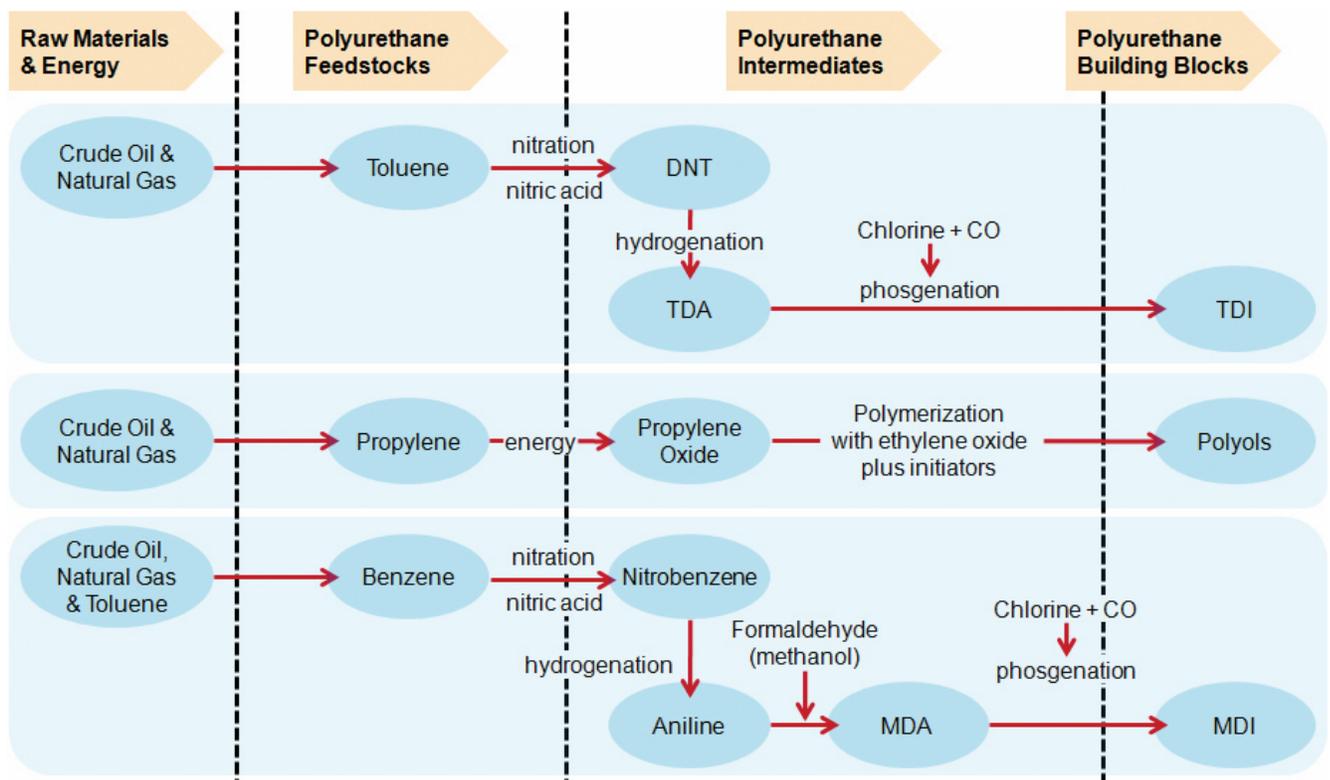


Figure 3. Steps in the production of TDI.

**Figure: 4 Physical Properties of Toluene Diisocyanate**

|   |  |  |
|---|--|--|
| Chemical Name                           | Toluene Diisocyanate<br>2,4-Toluene Diisocyanate<br>2,6-Toluene Diisocyanate | CAS No. 26471-62-5<br>CAS No. 584-84-9<br>CAS No. 91-08-7        |
| Synonyms                                |  | TDI, Toluene Diisocyanate  |
| Molecular Formula                       |  | CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> (NCO) <sub>2</sub> |
| Molecular Weight                        |  | 174.2  |
| Appearance                              |  | Clear, Colorless Liquid  |
| Odor                                    |  | Strong, Pungent  |
| NCO Content (wt%)                       |  | 48.2   |
| Specific Gravity at 25°/25°C (77°/77°F) |  | 1.22   |
| Density (pounds/gallon)                 |  | 10.2   |
| Viscosity (mPa s, cps) at 20°C (68°F)   |  | 3.2  |
| Boiling Point at                        | 10 mm Hg<br>760 mm Hg  | 120°C (248°F)<br>250°C (482°F)                                   |
| Freeze Point                            | 2,4 isomer<br>2,4/2,6 isomers (80/20 wt%)                                    | 22°C (72°F)<br>14°C (57°F)                                       |
| Vapor Density (Air=1)                   |  | 6  |
| Vapor Pressure                          | mm Hg at 25°C (77°F)<br>mm Hg at 35°C (95°F)<br>mm Hg at 45°C (113°F)        | 0.025<br>0.056<br>0.120  |
| Specific Heat                           | J/g K at 20°C (68°F)<br>J/g K at 100°C (212°F)                               | 1.46<br>1.71   |
| Heat of Evaporation                     | J/g at 120°C (248°F)<br>J/g at 180°C (356°F)                                 | 369<br>365   |
| Flash Point (DIN)                       |  | 135°C (275°F)  |
| Flammability Limits (V/V in air)        |  | LEL 0.9% UEL 9.5%  |
| Solubility in Water                     |  | Not soluble; reacts with evolution of CO <sub>2</sub>            |

TDI reacts with basic materials such as sodium hydroxide, ammonia, primary and secondary amines, and with acids and alcohols. Reactions with some of these products may be violent, generating heat, which can result in an increased evolution of TDI vapor, and the formation of CO<sub>2</sub>.

In general, TDI is not corrosive towards metals or other materials at room temperature. However, small amounts of rust or iron from mild steel containers may affect product quality. Mild steel storage containers can be lined to prevent discoloration.

TDI will attack and make brittle many plastic and rubber materials. Hoses made of these materials may experience cracking after only minimal usage.

A complete list of the physical properties of TDI is shown in Figure 4.

*Figure 4. Physical properties of Toluene Diisocyanate*

### 3. Health Considerations

#### Acute Hazards

TDI and products containing unreacted TDI are potentially hazardous materials. Therefore, a thorough knowledge of potential dangers, with strict adherence to recommended safety practices, is essential before TDI products are handled, stored, or used. Workers must be properly instructed and supervised in the handling of TDI. The primary hazard with TDI is the inhalation of its vapors. Limits have been established for allowable TDI vapor concentrations in the work environment.

In the United States, vapor levels of TDI are to be controlled according to standards established by the Occupational Safety and Health Administration (OSHA). The current OSHA permissible exposure limit (PEL) for TDI is 0.005 ppm as an 8-hour time-weighted average (TWA) concentration and as a ceiling concentration of 0.02 ppm. Other advisory groups have established guidelines for TDI exposure. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for TDI is 0.005 ppm as an 8-hour TWA concentration and 0.02 ppm as a STEL/ceiling limit. In two separate criteria documents, the National Institute of Occupational Safety and Health (NIOSH), has recommended that exposure to TDI be limited to 0.005 ppm as a TWA concentration for up to a 10-hour workday and a 40-hour workweek, with a ceiling concentration of 0.02 ppm for any 10-minute period.

In Canada, occupational exposure limits are regulated within each Province. The provinces have adopted exposure limits established by the ACGIH. Mexico has also adopted the ACGIH exposure limits. (0.005 ppm as an 8 hour TWA and 0.02 ppm as a 15 minute short term exposure limit).

Figure 5 is a partial list of exposure limits for TDI. The guidelines established by these agencies and groups represent current thinking and are believed to be conservative. There is no guarantee of absolute safety. Exposure guidelines are reviewed regularly and modified when new information dictates change. There is no data available indicating a concentration at which TDI vapor fails to produce adverse reactions in sensitized persons. Users of TDI must be fully informed on the most current guidelines and the regulations of all applicable authorities.

**Figure 5: Exposure Limits for TDI Vapors\***

| Country | Agencies and Groups | Exposure Limits     | ppm           |                           |
|---------|---------------------|---------------------|---------------|---------------------------|
| Canada  | ACGIH               | TLV<br>PEL          | 0.005<br>0.02 | 8hrs TWA<br>ceiling limit |
| U.S.A.  | ACGIH<br>OSHA       | TLV<br>PEL          | 0.005<br>0.02 | 8hrs TWA<br>ceiling limit |
| Mexico  | ACGIH               | TLV-TWA<br>TLV-STEL | 0.005<br>0.02 | 8hr TWA<br>15 min STEL    |

\*These values are subject to change and are given here only as examples of present limits.

- PEL                      Permissible Exposure Limit
- TLV                     Threshold Limit Value
- Ceiling Limit        Concentration that should not be exceeded
- STEL                   Short Term Exposure Limit (15 minute exposure)
- TWA                    Time Weighted Average
- ACGIH                American Conference of Governmental Industrial Hygienists
- COSHH                Control of Substances Hazardous to Health
- OSHA                  Occupational Safety and Health Administration

*Figure 5 - Exposure Limits for TDI Vapors*

#### Effects on the Respiratory System

Exposure to TDI above allowable vapor concentrations may cause irritation to the mucous membranes of the upper and lower respiratory tracts. Even very brief exposures to TDI vapors may cause difficult or labored breathing, throat dryness, headaches, and chest discomfort. Severe overexposure may result in bronchitis and pulmonary edema.

The symptoms of exposure may be delayed and an allergic reaction can appear in susceptible persons. The health of all personnel associated with the handling of TDI should be monitored regularly.

*Brief exposure to TDI vapors* may cause mild irritation and watering. The symptoms of direct contact to TDI liquid or high concentrations of vapors are severe watering, irritation, and inflammation of mucous membranes. Corneal opacity and discharge may result.

#### Effects on Skin

Skin contact with TDI may result in irritation and a mild tanning. Repeated or prolonged contact may cause redness, swelling, blistering, and burns. Direct contact may produce skin sensitization, contact dermatitis and eczema from repeated exposures. Animal studies indicate that TDI may induce respiratory hypersensitivity upon dermal exposure.

#### Effects on Ingestion

The effects of ingestion include the irritation and burning of the mouth, esophagus, and stomach. The harm that occurs will be a result of this irritation and not of any systemic toxicity.

#### **Chronic Hazards**

Exposure above the PEL may result in bronchitis, bronchial spasms and pulmonary edema. Long-term exposure to TDI has been reported to cause lung damage including reduced lung function that may be permanent.

Some individuals may develop a hypersensitivity to TDI vapors and may experience a severe reaction when exposed to TDI vapors at concentrations below established guidelines. Symptoms of hypersensitivity to TDI may include wheezing, shortness of breath, and difficulty in breathing. (See Sensitization)

A study by the National Toxicology Program (NTP) reported increased numbers of tumors in rats and mice dosed orally with TDI. However, a number of deficiencies have been cited which may compromise the validity of the study. A chronic inhalation study by CIVO indicated no increase in tumors in rats and mice when exposed to TDI at occupational levels.

In general, TDI is not anticipated to represent a significant cancer hazard when atmospheric levels are maintained below the recommended exposure guidelines.

#### **Sensitization**

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

The symptoms associated with respiratory sensitization by diisocyanates are those of asthma. Difficulty in breathing, chest tightness, wheezing, and coughing are common symptoms. If sensitized individuals continue to work with TDI, the latency period between exposure and onset of symptoms may be shortened, and the severity of the symptoms may increase. Many experts believe that early diagnosis of sensitization and removal from subsequent exposure can prevent permanent lung damage. Long-term, perhaps permanent lung damage and even death can result when sensitized individuals continue to have exposures to TDI. It is believed that cross sensitization may occur between different diisocyanates. Individuals who are sensitized to other diisocyanates may also demonstrate sensitization to TDI.

The PEL values and ceiling limits should be sufficiently low to prevent sensitization in most individuals. However, allergic reactions may occur in sensitized individuals at concentrations well below these values. Once sensitized, individuals are excluded from further exposure.

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

The odor threshold for TDI (0.2-0.4 ppm) is above the PEL value. TDI, therefore, has poor warning properties. The detection of TDI odor indicates overexposure. If anyone experiences an exposure severe enough to develop symptoms, no matter how mild, a physician should be consulted immediately.

## **First Aid**

### First Aid in Case of Inhalation

Affected persons should move from the contaminated area to fresh air supply immediately. Remove all contaminated clothing and contact medical personnel immediately. Keep affected persons comfortable and warm. Medication will rarely be necessary if adequate fresh air is immediately available.

If there has been a severe exposure and breathing stops, artificial respiration should be initiated immediately. If oxygen inhalation equipment is available, oxygen should be administered by a physician or authorized person. Never attempt to give anything by mouth to an unconscious person. Medication should be given only under the direction of an attending physician. In the event of breathing difficulty, a physician or authorized person should treat with medication to help prevent pulmonary edema.

### First Aid in Case of Eye Contact

In the event TDI comes in contact with the eyes, immediately flush affected area with running water for at least 15 minutes. The eyelids should be held apart during washing to ensure contact of water with all affected tissues of the eyes and eyelids. The affected person should receive medical attention, preferably from an eye specialist, as soon as possible.

### First Aid in Case of Skin Contact

Immediately move the affected person to a safety shower or other source of large amounts of water. Remove all contaminated clothing while under the shower and thoroughly wash affected areas with soap and water or propylene glycol for skin cleaning. Medical treatment should be given if irritation including redness, swelling, or a burning sensation persists. Launder contaminated clothing before reusing, and destroy in cases of severe contamination. In all cases, always take precaution against additional exposure from contaminated surfaces and materials.

### First Aid in Case of Ingestion

The affected person should immediately drink large amounts of water to reduce the concentration of the chemical. Vomiting should not be induced. The person should be transported to a medical facility as quickly as possible. If vomiting should occur, more water should be given immediately. Never give fluids or induce vomiting if the person is unconscious or having convulsions. Immediate medical attention should be provided.

## **Medical Considerations**

Preplacement evaluations should be performed on individuals being assigned to work with TDI. All personnel should receive a thorough health appraisal, emphasizing an examination of the respiratory tract.<sup>1</sup>

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

- Chronic diseases of the nose, throat, or lungs
- History of or presence of asthma or asthmatic bronchitis

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

## **Industrial Hygiene**

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

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

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

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

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

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<sup>1</sup> Tests may include but are not limited to pulmonary function or spirogram with emphasis on Forced Vital Capacity (FVC) and Forced Respiratory Volume (FEV 1-sec).

## 4. Safe Handling of TDI Products

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

### **Employee Training and Education**

The investment in employee education and training on proper storage and handling procedures for TDI is extremely important. Hazardous situations may be created by poorly trained personnel even in well-designed operations. All personnel that may come into contact with TDI products should be included in a Hazard Communication training program. Employee training and education programs must include the regulations of all applicable agencies. Local regulations must be obtained from the local authorities.

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

### **Engineering Considerations**

Building design considerations can reduce the potential hazards associated with the storage and handling of TDI. Careful consideration must be given to the design of the building's ventilation system. TDI vapors must be monitored and controlled below applicable regulatory limits. If possible, TDI should be processed within closed systems. When this is impractical, as in most slab foaming operations and laboratory areas, special consideration should be given to ventilation design.

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

The guidelines established by OSHA, ACGIH, NIOSH, leaflet M044 and others represent current thinking and are believed to be conservative and protective of occupational workers. There is no guarantee of absolute safety.

### Additional Precautions

Care should be taken to prevent contact of water with TDI. Water reacts readily with TDI and is the most common contaminant of diisocyanates. The hazard associated with this reaction is associated with the formation of CO<sub>2</sub> and the resultant increase of pressure in closed containers. Even small quantities of water can cause significant problems and the following safety recommendations must be observed:

- Store TDI in a dry environment using dry nitrogen or a dry air pad<sup>2</sup>
- Plug and cap all lines leading to and from storage tanks.
- Fittings and line connections should be maintained and stored in a dry environment.
- Do not tightly close any container of TDI that has been, or is suspected of having been, contaminated with water.

Contamination by basic compounds such as caustic soda, amines, or other similar materials must be avoided. The reaction of TDI with these materials may cause the generation of heat and CO<sub>2</sub>. The liberation of CO<sub>2</sub> in tightly closed or restricted vessels or transfer lines may result in a violent rupture.

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<sup>2</sup> Dry air or nitrogen should have a dew point below -40°C (-40°F).

## **Personal Protective Equipment**

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

### Eye Protection

Chemical safety goggles are required for all persons handling TDI. Cup-type or rubber-framed goggles equipped with the approved impact resistant glass or plastic lens are recommended. Cover-all type should be used for complete eye protection.

### Respiratory Protection

TDI vapor concentrations exceeding permissible exposure levels may occur. Such occasions included (but are not limited to) the following:

- The opening of tank car hatches, truck manway covers, or drum plugs
- Connecting or disconnecting of hoses and pipes
- Equipment operation or repair
- The breaking, or failure, of TDI piping or equipment
- Any spill or leak of TDI

No one should enter an area where TDI vapor concentrations may exceed the recommended exposure limits without appropriate personal protective equipment.

Personal protective equipment must be worn whenever exposure to TDI vapors is possible and should not be removed until adequate ventilation is confirmed.

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

If APR's cannot provide appropriate protection, respiratory equipment must be an air-supplied or self-contained breathing apparatus with full-face piece operating pressure-demand or other positive pressure mode.

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

### Head, Skin, Hand, and Foot Protection

Head protection should be worn to protect from falling objects, overhead leaks, and splashes. A long sleeved, impervious protective suit should be worn whenever there is possibility of exposure to TDI. Impervious gloves should be worn whenever the possibility of spills or splashes exist. Personnel handling TDI drums and cans should wear protective safety shoes with built-in steel toecaps. Rubber overshoes may be worn with ordinary work boots. Never wear uncovered leather shoes. Leather will absorb TDI, making decontamination of leather products such as gloves or shoes difficult.

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

**Fire Hazards**

Due to its high flash point (135°C/275°F), liquid TDI does not constitute a severe fire hazard. It is important, however, that the proper fire-fighting equipment be available in case it should be needed.

Water spray is effective for extinguishing fires covering large areas. Automatic sprinkler systems may be helpful in certain applications. When water is used to extinguish TDI fires, it should be applied in large amounts. Small amounts may only react with the hot TDI and worsen the fire situation. CO<sub>2</sub>, protein foam, or dry chemical extinguishers are also effective.

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

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

## 5. Shipment of TDI

Although TDI is a hazardous material in terms of reactivity and toxicity, it can be distributed and handled safely, provided that appropriate precautions are observed.

### Regulations

The shipment of TDI is subject to strict regulations within most countries in Europe and North America. In addition, the international movement of these products by road, rail or sea is subject to international agreements, which lay down specific requirements concerning shipment.

Figure 5 is a partial list of transportation regulations.

TDI is classified in all countries and internationally as UN2078, class 6.1, Packaging Group II, Symbol: Poison. Accompanying all shipments of TDI is an emergency response guide in North America or a Tremcard (transport emergency card) in Europe.

For shipments of TDI, BASF uses only professional transportation companies whose personnel are competent and well trained in the handling of TDI.

### Shipping Containers

TDI products are generally shipped in 250-kilograms (551 pounds) steel drums or in bulk. Bulk deliveries are generally made in tank trucks (road tankers) containing approximately 20 tons (44,000 pounds) or tank cars (rail tank wagons) containing up to 100 tons (approx. 220,000 pounds). Each container clearly displays a tag, placard, and/or label warning of potential hazards.

TDI containers must remain closed until use, to prevent moisture contamination. Only trained workers wearing the appropriate personal protective equipment are allowed to open containers of TDI. When a TDI container is opened, make-up dry air or nitrogen should be provided.

BASF has the responsibility to ensure that all TDI shipments leaving BASF facilities are properly prepared to comply with all the appropriate regulatory transportation requirements. Depending on the method of transportation, the rail carriers, truck lines or airlines are responsible for the safe shipment of TDI from the shipping point to the final destination. Emergency situations en route, such as accidents or leaking containers, must be reported immediately to appropriate regulatory authorities and to BASF.

**Figure 6: Transportation Regulations**

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

*Figure 6: Transportation Regulations*

### Unloading Operations

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

Written operating procedures covering all aspects of the unloading operation of TDI products must be prepared and available to all involved parties. All necessary personal protective equipment and emergency equipment must be available for the unloading operations. Personnel must be trained in the procedures and correct use of all protective clothing and emergency equipment (See Section 4).

### **Bulk Unloading**

Unloading of TDI products from bulk containers should be performed with a self-priming, seamless pump, and a vapor return line connected between the storage tank and the bulk delivery container. Dry nitrogen or dry air must be available to purge the unloading lines and vapor return line after unloading is completed. The storage tank must be equipped with a high-level device to stop the unloading automatically if the maximum tank level is reached.

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

The dimensions and physical arrangement of bulk containers vary; contact your local BASF representative for unloading (and loading) diagrams and procedures are available for MC-307 tank trucks and 20,000-gallon rail cars.

### **Drum Handling**

Drums should be handled and unloaded carefully to prevent damage. Operators must wear the proper personal protective equipment. Drums should be transported by lifting, to avoid damage caused by sliding or rolling. Only equipment designed for handling drums should be used. Forklift trucks equipped with "parrot beaks" or drum clamps are ideal. Each shipment should be closely examined for damaged or leaking drums. If leaking drums are found or damage occurs in movement, refer to Section 7 for procedures on proper handling of leaks or spills. Improperly equipped fork trucks may result in punctured or damaged drums.

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

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

Water contamination of drums must be avoided. This can result in a pressure build-up in closed containers by the generation of CO<sub>2</sub> gas from the water-TDI reaction. Drums showing evidence of pressure buildup must be vented immediately with caution, otherwise there is a potential for a violent drum rupture.

Refer to Section 6 for storage of TDI drums and Section 8 for recommendations on the neutralization and disposal of empty TDI drums.

### **Sample Shipments**

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

## 6. Storage

### **Storage and Handling Considerations**

A thorough knowledge of the chemical and physical properties, federal and local regulations, and building codes, is necessary for the safe handling and storage of TDI.

TDI is not considered a corrosive chemical; however, the selection of materials for TDI handling systems plays a crucial role in maintaining TDI product quality. Trace amounts of metals, including iron (rust), copper, brass or aluminum, may affect the reactivity of TDI in sensitive applications. In general, mild steel, epoxy-phenolic lined steel, or stainless steels are the recommended materials of construction for TDI handling and storage systems. If unlined mild steel is selected, the surface must be maintained clean and rust-free to maintain product quality. Presently, plastic materials are not recommended for handling TDI. TDI may migrate into some plastics causing them to become brittle with age.

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

The reaction of TDI with moisture, even from ambient air, will produce polyurea solids and CO<sub>2</sub>. These insoluble polyureas will deposit on surfaces of pipes and tanks causing line restrictions and filtration problems. The generated CO<sub>2</sub> could present a pressure hazard, including the potential of a violent rupture of an under-vented tank or vessel.

Although TDI is relatively non-flammable (flash point 135°C/275°F), TDI should not be stored adjacent to highly flammable materials. Water, dry chemical, protein foam, or CO<sub>2</sub> fire extinguishers should be available in all storage and processing areas. Automatic fire or smoke detection equipment, as well as automatic sprinklers should be installed in all TDI processing and storage areas.

### **Storage Tank Design**

All TDI storage tanks must be blanketed with nitrogen or dry air.<sup>3</sup> Storage tanks should be maintained under a slight pressure (1mbar/1-2 psi). Storage tank vents must be sized to adequately protect the tank against pressure buildup during unloading operations or the generation of pressure from moisture contamination. As a minimum, TDI vents must be directed outside, away from ventilation systems, or into plant exhaust vent systems. Activated carbon filters have been successfully used to reduce TDI emissions from storage tank vents. In all instances, TDI venting procedures must comply with applicable codes, regulations and permits.

To maintain the desired product temperature, TDI storage tanks should be equipped with a temperature indicator, heat tracing, and insulation. The preferred method of temperature control is external heat exchangers using an inert heating medium.

External tempered water or electric tracing has been successfully used. Steam should not be used due to the possibility of overheating. Water must be prevented from having the opportunity to contact TDI. To eliminate any potential of a coil leak, internal coils are not recommended. Heating coils and heat exchangers should be checked for corrosion regularly.

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<sup>3</sup> Dry nitrogen or dry air must have a new dew point below -40°C (-40°F).

The TDI storage tank temperature should be maintained between 18°C (65°F) and 41°C (105°F) to ensure consistent product quality. At extended periods above 41°C (105°F), TDI may begin to discolor and dimerize. At extended periods above 100°C (212°F), TDI may begin to trimerize; the trimerization reaction is exothermic and will generate CO<sub>2</sub> gas, which may create a pressure hazard in a sealed or under-vented vessel. If TDI is shipped or stored below the recommended storage temperature, freezing or partial freezing may occur. TDI can be easily reliquified without any degradation by heating 23-35°C (73-95°F). Always be certain that all of the TDI has reliquified and that the product is thoroughly mixed. The 2,4- isomer has a higher melting point than the 2,6- isomer. Unless the TDI is thoroughly melted and mixed, the liquid isomer ratio may vary. Off ratio TDI may produce processing problems because the reactivities of the isomers vary.

TDI tanks should be equipped with level indicators and separate high level alarms as well as cutoffs to prevent accidental overflow. Tank areas must be diked to prevent runoff in the event of TDI release. Diking must be sufficient to contain potential spills and leaks and prevent accident release of TDI into sewers, waterways or public thoroughfares. Dikes must be designed for 1 ½ times the tank capacity, or as directed by codes and regulations for handling hazardous chemicals. Storage tanks should be designed to hold an entire shipment (i.e., if the shipment is typically a 20,000-gallon rail car, the tank capacity should be greater than 20,000 gallons).

Transfer pumps should be of compatible materials and of a seamless design. Canned pumps and magnetic drive pumps have been successfully used. Appropriate hazard labels may be required on storage and transfer systems containing TDI. In the United States, OSHA requires hazard communication labels for all containers containing TDI.

### **Drum Storage**

Drum storage areas should be covered and well ventilated. Ideally, TDI drum storage areas should be diked and separated from materials reactive with TDI. Local codes may have specific requirements for the storage of hazardous chemicals.

All storage areas should be arranged in an orderly manner, leaving doorways and exit routes clear.

## 7. Emergency Procedures

### **Guidelines for Dealing with TDI Product Incidents**

All incidents tend to be unique, and it is not possible to write guidelines to deal with every circumstance. Each incident must be assessed from the information available.

All people involved with handling or transportation must be aware of the hazards associated with TDI, the appropriate emergency procedures, and their individual responsibilities in the event of an emergency. The primary response to any release of TDI, whether a transportation incident or an in-plant spill, is to evacuate all unprotected people to a safe location. Only then should properly protected and trained personnel evaluate, contain, stop, clean up, and decontaminate any spill.

Depending upon the size, location and type of release, government agencies or authorities may require notification. In the United States, transportation incidents involving TDI must be reported to the National Response Center (NRC) (1-800-424-8802) for any release over the reportable quantity of 100 lbs. (approximately 10.0 gallons). This is a requirement of (U.S.A.) Federal CERCLA regulations.

Any release to the environment of over 100 lbs. must be reported to the NRC and the local planning commission as outlined under EPCRA regulations (U.S.A.). Regulations involving the release of hazardous chemicals is continually evolving, therefore, it is important that all companies handling TDI be aware of the current legislative requirements in each jurisdiction.

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

The odor threshold of TDI is above the established exposure limits for TDI. Areas should not be considered free of diisocyanate vapors until the area has been monitored.

### **Spills and Leaks**

Only properly trained and equipped personnel (see Section 4) should attempt to clean up spills and leaks. The spill should be contained and the leak stopped to prevent further contamination.

It is necessary to distinguish between minor incidents, that may occur in a laboratory or a workshop handling TDI regularly, and major spills involving, for example, a bulk tank truck. The most important criterion for distinguishing between the two is the ability of the personnel on the spot to deal with the occurrence, rather than the actual size of the incident.

#### Minor Incidents

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

Use more than enough absorbent material to absorb all of the liquid TDI. Shovel or scoop the absorbent into another open top container and remove it to a safe location for neutralization. Do not tightly seal this container since the TDI will react with any moisture present and generate CO<sub>2</sub> gas. This could cause a sealed container to burst. After the drums are moved to a safe area, fill the container with an appropriate neutralizing solution and allow it to stand at least 48 hours. After 48 hours, the container may be closed. The container should remain vented, however, to prevent any pressure buildup. The contents of the container should be properly disposed of (See Section 8).

After the absorbent has been shoveled from the spill site, the site should be washed and scrubbed down with a liquid neutralizer. Once the area is clean, it should be tested for diisocyanate vapors. If TDI vapors continue to be present, the decontamination should be repeated until the area is free of TDI vapors.

Decontaminating or neutralizing solutions are mixtures of agents that react with the TDI and agents that promote the reaction. The choice of solution will depend on the location (inside or outside), temperature (below or above freezing) and the flammability requirement for the intended use. A typical decontaminating solution can be made by mixing water (90-95 vol %), household ammonia (3-8 vol %) and liquid detergent (1-7 vol %). The water and ammonia will react with the TDI to form polyurea solids and CO<sub>2</sub> gas, while the ammonia and detergent help promote the reaction. This solution works well indoors at normal room temperatures. Solid neutralizers, which are neutralizers premixed with an absorbent, may be used for the quick clean up of very small spills. It is important to note the hazards and regulatory limitations of any neutralizing hazards and regulatory limitations of any neutralizing solution. Ammonia may be regulated as a hazardous material. Before using ammonia, refer to any exposure limits and applicable regulations. The use of sawdust in combination with any decontaminate solution may cause auto-ignition.

### Large Spills

For large spills of TDI, a “state of emergency” must be declared as noted in the Risk Management Plan. This may require notification of local emergency response services such as the fire department. Such a possibility should be factored into every TDI user’s community awareness program.

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

Once the spill has been isolated and contained, the appropriate clean-up procedures should be used to remove or decontaminate the TDI. For specific instructions or assistance, the BASF emergency help line is available 24 hours a day in the United States (1-800-832-HELP) or in Germany (0-621-6043333).

For transportation incidents in the United States, the Chemical Manufacturers Association (CMA) operates CHEMTREC.

**Figure 7: Emergency Response Networks**

| <b>National Emergency Systems</b>                   |          |                    |
|---|----------|--------------------|
| Canada  | CANUTEC  | +1 (613) 996-6666  |
| U.S.A.  | CHEMTREC | +1 (800) 424-9300  |
| <b>BASF Emergency Systems</b>                       |          |                    |
| BASF Corporation (U.S.A.)                           |          | +1 (800) 832-4357  |
| BASF Ludwigshafen (Germany)                         |          | +49 (0621) 6043333 |
| BASF Schwarzheide (Germany)                         |          | +49 (035) 75262312 |
| BASF Company Ltd. (Korea)                           |          | +82 2 3707 7770    |
| Shanghai BASF Polyurethanes Co. Ltd. Caojing, China |          | +86 21 5861 1199   |

*Figure 7: Emergency Response Networks*

The CHEMTREC number (1-800-424-9300) is available 24 hours a day and is on all BASF Bills of Lading and MSDSs. A call to CHEMTREC will set the emergency response notification process in motion and provide emergency response information to response personnel. In other countries, emergency response networks for handling hazardous chemical emergencies have been established. Figure 7 is a partial listing of emergency response networks.

### **TDI Involved in Fires**

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

- a) large quantities of water
- b) dry chemical powder
- c) protein-based foam
- d) CO<sub>2</sub> extinguisher

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

The use of water or foam to extinguish the fire and cool the container makes it likely that moisture will enter the damaged tank or drum. Since water reacts with TDI to form solid polyureas and CO<sub>2</sub>, the danger exists that after the damaged area is plugged, a pressure buildup can occur. To prevent damage to the tank, it must be vented.

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

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

### **Pressurized Drums**

A bulging drum of TDI should be assumed to be the result of contamination of the product, usually with water. This slow but unstoppable reaction produces CO<sub>2</sub>, which increases the pressure inside the container. Since it is not easy to judge the acute risk of bursting, the drum under pressure should be left where it is. A tarp should be placed over the drum.

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

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

### **Chemical Reactions**

The combination of polyol and diisocyanate components yields large amounts of heat and probably gas evolution. The reaction, once begun, cannot be stopped and the goal must be to prevent pressure buildup by venting. In most instances, a controlled venting via the safety valve may not be possible because the safety valve may become plugged with foam or solids. If possible, stop uncontaminated material from entering the reaction by pumping it into a separate vessel.

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

An evacuation of the immediate surroundings should be considered because of the potential large amounts of heated TDI vapors that can be evolved. All personnel involved must wear complete protective equipment.

## 8. Environmental Considerations

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

### **Disposal of Waste TDI**

Waste TDI products are hazardous materials and must always be disposed of in accordance with local and federal pollution control regulations. There are three basic methods for disposing of liquid TDI wastes. The choice of method will depend in part on the amount of waste to be treated and the availability of decontaminates. In the United States, TDI treatment and disposal are regulated under the Resource Conservation and Recovery Act (RCRA). Under RCRA, any facility generating more than 1000 kilograms (2,205 pounds) of hazardous waste per month must obtain a permit from the Environmental Protection Agency (EPA) to treat TDI products for disposal.

#### Method 1: Reaction with Waste Polyol

React with activated waste polyol to make a low quality polyurethane foam which can be sold or used as a manufactured product. If the foam produced is to be disposed of, all regulations must be adhered to. In the United States, all foam produced in this manner for disposal is classified as "Hazardous Waste," regulated under RCRA. In Europe, such foam, if free of unreacted components, can generally be incinerated or disposed of as normal house waste in an authorized waste disposal area. This method should only be used when a correct stoichiometric mixing can be guaranteed. Improper mixing will leave a product containing unreacted TDI or polyol.

#### Method 2: Reaction with Liquid Decontaminates

The waste TDI product should be added slowly and stirred into the liquid decontaminates (See Section 7 for preparation of decontaminate) in an open-top container. TDI should be added to the decontaminate. Adding the decontaminate solution to the TDI may produce excessive heat! The amount of TDI product to be treated should not exceed 10% of the amount of decontaminate used. Leave the treated drum for 48 hours in a properly ventilated area; this will remove the toxic hazard. Decant the liquid and dispose of both the liquid and solid material according to all local and federal regulations. The decontamination products are classified as hazardous wastes in the United States and generally in Europe.

#### Method 3: Incineration

Incineration under approved, controlled conditions is the preferred method for all but small amounts of TDI product. It should, however, only be done in properly supervised equipment specifically designed for the disposal of noxious chemical wastes and properly permitted by the local and federal agencies.

### **Decontamination and Disposal of Used Containers**

TDI products may be delivered in drums. These drums are designed to be one-way packages and cannot be returned to the suppliers.

Residual TDI product will remain in the drum until it has been completely emptied. Local and federal regulations vary concerning the disposal of empty containers. Empty TDI drums are potentially hazardous and should, therefore, only be handled by trained personnel. Personnel should be trained to empty TDI drums completely. In the U.S.A., RCRA regulations classify drums as empty if less than one inch of liquid remains. All TDI drums, after being well drained, should be decontaminated with a prepared decontaminate solution using the following procedure:

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

- b) Leave drum standing unsealed for at least 48 hours to allow complete reaction. Sealing of the drum must be avoided to prevent pressure buildup by evolved CO<sub>2</sub>.
- c) Pour out liquid decontaminate into a storage vessel. This solution can be used several times.<sup>4</sup>

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

If decontaminated drums are to be disposed of, they should be punctured to prevent reuse. Independent of the method used, cleaned TDI drums must not be used for the storage of food or animal feed. Comply with all local and federal regulations with when cleaning and disposing of empty TDI drums.

Some nations allow well-drained drums to be sent to a permitted reconditioner without being decontaminated. If this is allowed, the drums must be labeled analogous to the filled ones and all closures must be tight to prevent water contamination. Water contamination can cause CO<sub>2</sub> gas to be evolved, which could pressurize the drum and create a serious hazard.

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

### **Ecological Effects**

Environmental toxicity test data is reported as follows:

Daphnia magna, 24 hr LC50  
->500 mg/L Practically nontoxic

Zebra Fish, Static 24 hr LC50  
->500 mg/L Practically nontoxic

Redwing Blackbird, Oral LD50  
- 100 mg/L Not appreciably toxic

The reaction products of TDI and water are not biodegradable but chemically inert (See Guidelines for the Distribution of TDI and MDI, ISOPA).

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<sup>4</sup> There are two disadvantages to using this simple method. The resulting crust can conceal unreacted diisocyanate, especially in the case of drums not having been adequately drained. Furthermore, it is difficult to remove the crust from the walls of the drum.

## 9. References

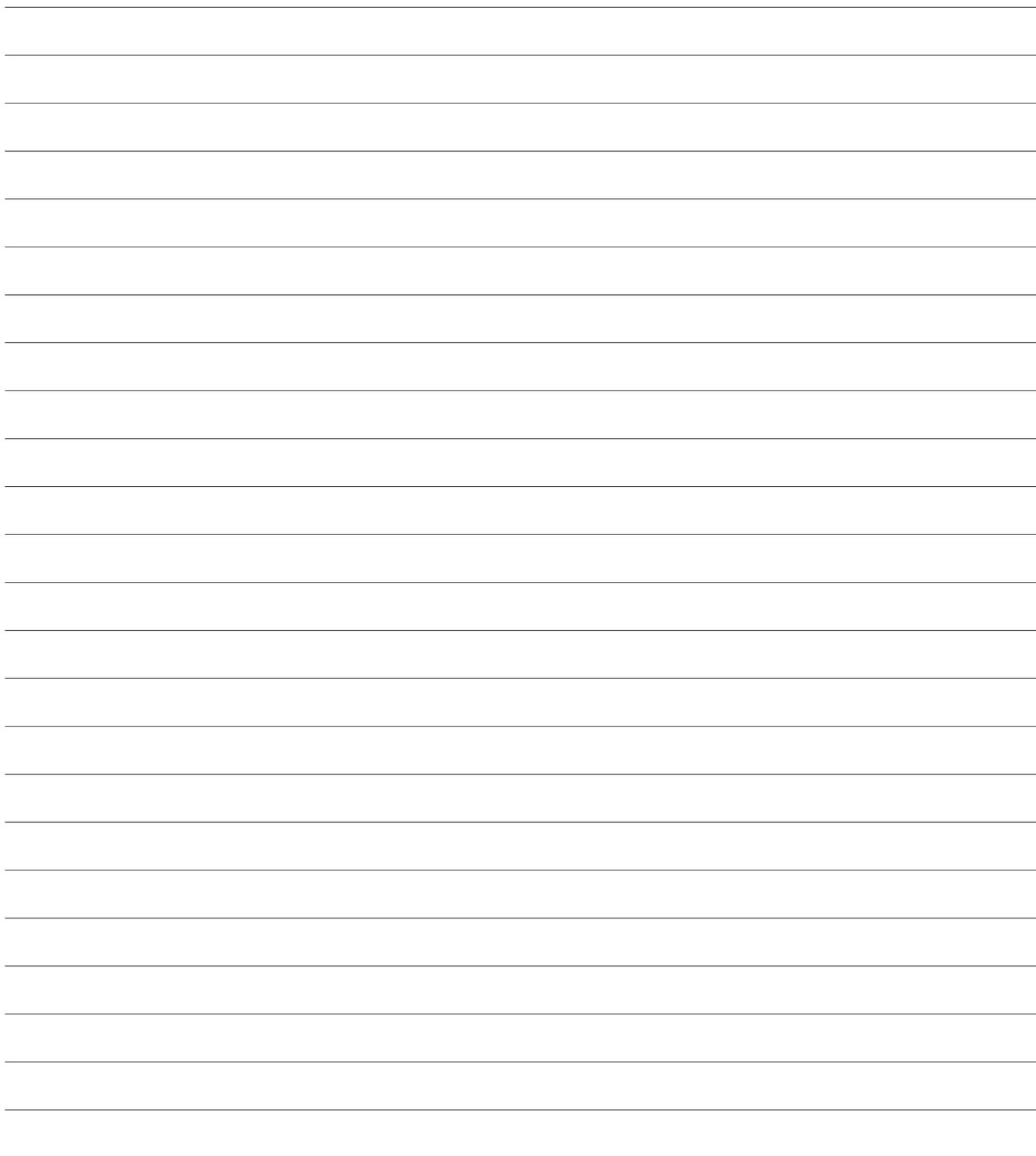
Among others, the following literature has been used for this TDI Manual:

|              |   |
|--------------|---|
| ( 1 ) BRMA:  | Toxicity and Safe Handling of Diisocyanates and Ancillary Chemicals, A code of Practice for Polyurethane Flexible Foam Manufacture (July 1991)  |
| ( 2 ) CIA:   | Guidelines for the Reception and Bulk Storage of TDI and TDI (Aug. 1989)  |
| ( 3 ) ISOPA: | Guidelines for the Distribution of Toluene Diisocyanate (TDI) and Diphenylmethane Diisocyanate (MDI) (2001)<br><br>Guidance on the Seveso Directive and its Application to Polyurethane Manufacturers (Sept. 1991)<br><br>European Isocyanate Producers Association<br>4 Avenue Van Nieuwenhuyse B-1160 Brussels, Belgium<br>Tel. (02) 676 74 75  |
| ( 4 ) CPI:   | Hyperactivity and other Health Effects of Diisocyanates: Guidelines for Medical Personnel (2004)<br><br>Drum Handling Information Kit (2001)<br><br>Center for the Polyurethanes Industry of the American Chemistry Council<br>700 Second Street, NE<br>Washington, DC 20002<br>Tel. (202) 249-7000<br>Fax (202) 249-6100<br><a href="http://www.polyurethane.org">www.polyurethane.org</a> |

## 10. Other Considerations

The regulations for handling toluene diisocyanate as well as other hazardous chemicals are continually evolving. Also, regulations and procedures vary widely from country to country. The body of this publication contains general information for handling toluene diisocyanate.





## BASF - The Chemical Company

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