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EUROPEAN DIISOCYANATE & POLYOL
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PRODUCERS ASSOCIATION

GUIDELINES

for Safe Loading / Unloading Transportation Storage of TDI and MDI in Bulk

www.isopa.org

Foreword

The second revision of these Guidelines, dated February 2006, has been thoroughly reviewed by ISOPA's Logistics EHS Working Group under chairmanship of H. van Wijnen (Huntsman).

The intention is to contribute to overall safety standards by updating these Guidelines and adding numerous topics to address the comments received and experience gained over the past 4 years.

Please note that asterisks (*) have not been used to indicate updates because there are a lot of changes. Indeed, this third revision should be regarded as a complete revision.

I would particularly like to thank my colleagues in the Working Group for their commitment and co-operation:

S. Beddegenoodts - Dow
R. Magliocchi - Shell
N. Meijboom - Shell
R. Vieler - Bayer

H. van Wijnen
Chairman

Preface to the Third Revision

The main changes contained in this third revision are as follows:

Removal of data from Chapter 2 that can be easily found on the producer's Safety Data Sheet, e.g. classification and labelling, hazard statements, signal words, transport classification.

- Removal of chapters on Transport by Rail and Transport by Sea or Inland Water.

- Addition of a chapter on Storage.

- Addition of sections within chapters on:
  - Non Standard Operations (NSO)
  - TDI / MDI and Polyol in adjacent compartments
  - 80/20 rule
  - Fall protection

- Complete review and edit of other content including rephrasing for:
  - Fall protection
  - Markings for vapour, liquid and pressure connection
  - Sample tube
  - Sizing of vapour return hose
  - Opening of tank containers and the "Do not open the manlid" sticker

An appendix is added describing the chemistry of the reaction of isocyanates with water.

Contents

1 Introduction

1.1 Purpose

These Guidelines have been prepared by ISOPA (the European Diisocyanate & Polyol Producers Association), a sector group of CEFIC (the European Chemical Industry Federation), to establish appropriately high levels of safety for the loading / unloading, transportation and storage of toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

Whilst MDI is classified and regulated as hazardous only for use and TDI as hazardous for both use and transport, they can be handled and shipped safely provided that appropriate precautions are observed.

1.2 Products

Reference is made throughout these Guidelines to TDI and MDI and to their variants and preparations to the extent that products are classified as TDI and MDI. Preparations containing solvents are not covered by this document.

The decision of the UN Committee acknowledges that MDI does not meet hazard conditions for inclusion in Hazard Class 6.1. However, MDI quite properly continues to be regulated in EU countries as a hazardous material in handling and usage (see Chapter 2). For this reason, it has been decided to continue to treat MDI in these Guidelines. To avoid the need for repeated explanations in the text of the Guidelines, wherever MDI is referred to as a hazardous material it should be understood in this sense.

1.3 Scope

These Guidelines cover important aspects of loading, unloading, transportation and storage activities of TDI and MDI in bulk from loading to delivery point. They deal with bulk transport units such as road tankers, isotanks and swap-body containers. Reference to existing regulatory controls is only made where this is considered necessary for the purpose of clarification.

These Guidelines do not deal with the bulk movement of TDI / MDI in ocean-going chemical tankers, inland waterway barges and rail tank cars.

1.4 Transport Safety

It is strongly recommended that TDI and MDI producers arrange transport with approved carriers (e.g. SQAS assessed or similar system).

All carriers should train their drivers who transport TDI and / or MDI using the ISOPA driver training package (**www.isopa.org / logistics EHS / driver training**).

Customer collection of TDI / MDI is not advised. If unavoidable then only carriers participating in the ISOPA driver training program should be used.

1.5 Adoption

ISOPA recommends these Guidelines to be adopted by all parties who are involved in the transport and distribution of TDI / MDI.

It is the individual responsibility of users of these Guidelines to evaluate and apply them taking all specific circumstances and their own situation into consideration.

No part of these Guidelines may be used or interpreted in a way that conflicts with existing international and / or national legislation. In all circumstances, applicable regulatory and legal provisions will always take precedence over these Guidelines or any part thereof.

2 Main Properties, Hazards and Safety Information

(For more details see the producers' Safety Data Sheets)

In practice, TDI is sold as 100% 2,4-isomer or as 80/20 or 65/35 mixtures of the 2,4-and 2,6-isomers, and MDI in both its monomeric and polymeric forms. Variants and preparations of TDI and MDI are also produced.

2.1 Appearance

2.1.1 TDI

	Liquid		*Reacted*	
TDI	Clear to pale yellow sharp, pungent		White, foamy	

2.1.2 Polymeric MDI

	Liquid		*Reacted*	
MDI	Brown, slightly musty		Brown, crusty	

2.1.3 Monomeric MDI

	Liquid		*Reacted*	
MDI	Clear to pale yellow sharp, pungent		White, foamy	

2.2 Main Physical / Chemical Hazards

TDI / MDI are NOT inherently explosive, nor are they oxidisers, or spontaneously flammable in air or flammable at ambient temperature (note the flash points). However, the following points must be noted:

Water

TDI / MDI react with water to produce carbon dioxide and a biologically and chemically inert solid, known as a polyurea. While this is not in itself a dangerous reaction, it can lead to the development of excessive pressure inside closed containers. Eventually, this may even burst the tank container shell should the TDI / MDI be contaminated with water. If no corrective action is taken the reaction will become more violent. The chemistry of the reaction of isocyanates with water is described in Appendix 1. The reaction with water is accelerated by other chemicals as described below.

Other chemicals

The contamination of TDI / MDI with other chemicals must be avoided at all times!
TDI / MDI react with other chemicals such as acids, alcohols, alkaline materials (e.g. caustic soda, ammonia), and other chemicals that contain reactive groups. The reaction may generate heat resulting in an increased evolution of TDI / MDI vapour and the formation of carbon dioxide.

Rubber and plastics

TDI / MDI will attack and embrittle many plastics and rubber materials within a short period. Although this is not dangerous in itself, it may lead to cracking, for example of hoses and protective clothing. Particular care should be taken to ensure that your liquid tight gloves (see section 3.1) do not contain any cracks caused by TDI / MDI embrittlement.

In a fire

TDI and MDI have high flash points. However, in a fire - if heated up enough to generate sufficient vapour for ignition - they will burn, giving off volatile substances, which are hazardous if inhaled.

TDI / MDI in a closed container exposed to the heat of a fire will decompose with a build-up of pressure resulting in the risk of the container bursting.

2.3 Health Hazards and First Aid

Chemicals can present a health hazard by inhalation, skin / eye contact or by swallowing. For TDI / MDI, inhalation exposure to the vapour, aerosol and/or dust is the greatest concern by far.

Inhalation

Exposure to the vapour, aerosol and / or dust of TDI / MDI will irritate the membranes of the nose, throat, lungs and eyes. Several symptoms might follow, which may include: watering of the eyes, dryness of the throat, tightness of the chest (sometimes with difficulty in breathing), and headaches. Hyper-reactive or hypersensitive people can experience bronchoconstriction (asthmatic signs and symptoms), which can be fatal if not treated immediately.

The onset of the symptoms may be delayed for several hours after over-exposure has taken place. In people who have developed an allergy to TDI / MDI, by a single or repeated exposure, very low concentrations may lead to asthmatic signs and symptoms. These people must avoid handling TDI / MDI.

In case of inhalation remove exposed persons to fresh air and give artificial respiration if not breathing. Keep under medical observation for at least 48 hours.

Eye contact

TDI / MDI in the form of vapour, aerosol or dust irritates the eyes, causing watering and discomfort. Splashes of liquid TDI / MDI in the eyes could cause severe irritation if not immediately washed out with large amounts of water for at least 15 minutes. Medical attention should be obtained. Protective equipment must be worn as described in Chapter 3. Drivers and operators should not wear contact lenses when handling isocyanates, but should wear glasses instead.

Skin contact

TDI / MDI may cause irritation to the skin. In case of skin contact, the affected skin should be washed with warm water (and soap). Contaminated clothing should be removed immediately.

Swallowing

These products may cause severe irritation to the mouth and stomach if swallowed. If swallowed, do not induce vomiting. Wash out the mouth with water and spit it out. Do not swallow the water. Obtain medical attention immediately.

Long-term health effects

Inhalation and skin contact may cause sensitization. Chronic exposure by inhalation may result in permanent decrease in lung function.

Industrial experience in humans has not shown any link between TDI / MDI exposure and cancer development.

More safety information

For more safety information, consult the supplier's safety data sheets for TDI / MDI.

3 Personal Protective Equipment

AII necessary protective clothing and emergency equipment should be available for loading and unloading operations. Persons should be trained in the correct use of this clothing and equipment. Whenever the driver leaves his vehicle he should wear the minimum required personal protective equipment as a precaution in case of an emergency.

3.1 Recommended Personal Protective Equipment to transfer TDI products

The minimum personal protection to be worn by plant personnel and drivers when handling TDI should be:

- Hard hat
- Full face mask (with appropriate filter)
- Liquid-tight gloves
- Safety shoes / boots
- Full chemical suit
- Safety harness (if required)

For information concerning the appropriate protective material contact your supplier. If, as in the case of TDI or heated MDI, there is an increased probability of inhalation of TDI / MDI vapour, for example, during sampling or the connection / disconnection of pipeline or flexible hose joints, then an approved respirator must be worn. This should be a full face mask respirator with filter suitable for organic vapours and particles (minimally, AP2).

3.2 Recommended Personal Protective Equipment to transfer MDI products

The minimum personal protection to be worn by plant personnel and drivers carrying out this operation should consist of:

- Hard hat
- Goggles
- Liquid-tight gloves
- Safety shoes / boots
- Overall
- Safety harness (if required)

3.3 Emergency Equipment

Drivers should always have an eyewash bottle in the vehicle. The industry standard for loading / unloading sites is to have an emergency shower and eyewash available close to the discharge location. In case of an emergency (e.g. a TDI or MDI loss of containment), especially at elevated temperatures, the protective equipment described under sections 3.1 and 3.2 should be worn by all persons dealing with the incident. For large spills the use of self contained breathing apparatus and impervious suits is strongly recommended.

4 Design and Construction of Bulk Transport Equipment

4.1 Bulk Transport Equipment

It is strongly recommended that tanks and ancillary equipment are constructed of stainless steel for ease of cleaning and to minimise product deterioration.

4.1.1 Top fill and Top discharge

The product characteristics of TDI and MDI are such that tanks must be equipped for top fill and top discharge only. Thus, the fittings must be positioned on the top of the tank and not at the bottom because:

- Valves positioned underneath the level of the product become more sensitive to malfunction due to moisture ingress
- The risk of spills occurring between loading and unloading point is reduced
- The risk of damaging the fittings during handling (containers) and driving is much lower
- There is an additional advantage from a security point of view as it is more difficult to tamper with the product

All tank openings should be sealed.

4.1.2 Road Tankers, Isotanks and Swap Bodies

Road Tankers, isotanks and swap-bodies used for the carriage of TDI / MDI must meet the design and construction requirements of national and international regulations (e.g. ADR & IMDG).

In addition, the frame of isotanks and swap-bodies must comply with the International Convention for Safe Containers (CSC) and operated using an Accepted Continuous Examination Program (ACEP).

The use of multi-compartment road tankers or tank containers for TDI / MDI is not recommended because it increases the (handling) risks during loading / unloading operations.

4.1.2.1 Fall Protection

Where work on top of transport equipment is necessary, no persons are permitted to carry out this work at an elevation unless they:

1. have the required training and
2. are protected from falls at all times. They may be protected via:
   a. Fall prevention: In practice this is most commonly achieved by erecting a gantry with 360° guard rails. A single collapsible handrail is not considered as adequate fall protection and is considered as hazardous.

b. Fall restraint systems: In practice this is most commonly achieved by movement restriction. Attaching a movement restriction belt to the collapsible handrail of the transport equipment is not adequate and is considered as hazardous.

c. Fall arrest systems: In practice this is most commonly achieved by attaching a full body fall arrest harness with a short lanyard to a fixed anchorage point or to a horizontal lifeline system or sliding beam anchors. A fall arrest harness attached to the collapsible handrail is not an adequate fall arrest system and is considered as hazardous.

When looking to reduce fall related incidents and consequences thereof, the first measure to consider is the avoidance of work on top of transport equipment. This can be achieved partially by introducing ground operated tanks, but not for Diisocyanates where top loading and unloading is required for security and quality.

If a 360° guard rail is provided, the maintenance and training should be provided by the site where the activities take place. This is an effective means to prevent falling. However, such guard rails are hard to adjust to non-standard transport equipment and will not be available at locations that are sporadically used.

If no permanent fall prevention guard rail can be provided, falls can be prevented by providing mobile stairways:

1. these are adjusted / adjustable to the height of the transport equipment
2. these do not interfere with overhead structures
3. these can be readily put in position (consider weight and surface)

If the above options are exhausted, fall arrest can be considered as a final solution. The following restrictions apply:

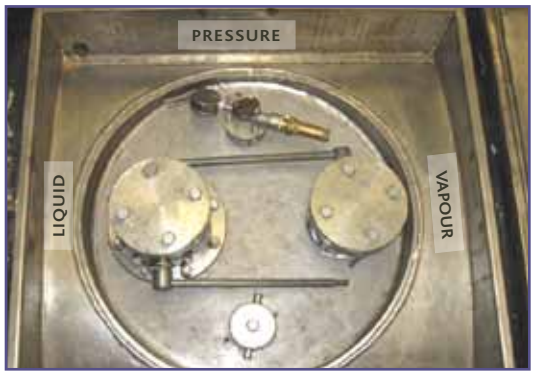
1. The anchor point provided at the site has to be inspected periodically according to the manufacturer's instructions.
2. Evacuation from the arrest must be taken into account using quick release lanyard or by self retracting – slow descent lanyard.
3. Access to the top of the transport equipment is preferably by stairs with handrail. If a ladder is used, both hands must be free. The fall arrest lanyard is secured before transferring from the platform / ladder to the top of the transport equipment. If a vertical ladder at the back of the truck/container is used, the harness needs to be attached to a retractable lanyard before climbing the ladder.
4. The rescue operation needs to be analyzed at the site where the operation takes place. This requires that the operation is not carried out unattended. Rescue must be carried out within 5 minutes of the fall to prevent suspension trauma.
5. Correct usage of the harness is essential. Training should be provided by the organization providing the harness to the employee. The training should include instructions on inspecting the harness before every use. If the driver has his own harness the training is organized by the carrier. If the driver is handed a harness at the site, the site organization will provide and document the training. That organization is also required to inspect the harness and lanyard in accordance with the manufacturer's instructions.

4.1.3 Road Tankers and Isotanks Equipment

In addition to the standards required by regulations cited under 4.1.2, road tankers and isotanks must be designed and constructed to meet the following construction factors:

4.1.3.1 Couplings, Openings and Ancillary Equipment

It is recommended that liquid, vapour return and pressure connections on all tanks / vehicles are clearly labelled.



The dip pipe connection should be marked with "LIQUID" and the vapour return connection with "VAPOUR". Markings should be on an engraved plate as close as possible to the connection. It is recommended to also mark the air pressure connection (claw coupling) with "PRESSURE". As a minimum, the language on the engraved plates should be English.

All couplings must be secured by a blind flange or protective cap and appropriate gasket or another system providing equal protection (dry disconnect coupling).

The following fittings must be available:

Manhole - minimum diameter 450 mm with hinged swing bolts. The manlid should be labelled with a "DO NOT OPEN THE MANLID" sticker.

Dip pipe and vapour return - via a DN50 valve fitted with a DN50 4-bolt flange with a Pitch Circle Diameter (PCD) of 125 mm. Preferably, it should be stud mounted.

Pressure connection - via a 25 mm threaded connection or claw coupling, the latter is preferred.

Optionally, a cleaning aperture (fist-hole) designed in accordance with the requirements of ADR may be fitted to the lower part of the shell.

Temperature indicators for each compartment are required and should be regularly checked.

In addition, it is recommended that a manometer to check the pressure inside the tank be installed.

4.1.3.2 Pressure Relief and Vacuum Valves

Combined pressure relief / vacuum valves are not allowed. These valves can become stuck with solidified product as these cannot be fitted with a rupture disc.

4.1.3.2.1 Pressure Relief Valves - Road Tankers

Fitting of pressure relief valves on road tankers is not compulsory. A direct pressure connection on top of the tank is prohibited when the tank is not fitted with pressure relief valves for discharging under pressure. A connection using a fixed pressure line fitted with a pressure relief valve must be used. If the road tanker is fitted with pressure relief valve(s), the valves must be preceded by bursting disc(s) and manometer(s) to indicate disc rupture.

4.1.3.2.2 Pressure Relief Valves - Tank containers

Tank containers should be fitted with pressure relief valve(s) preceded by bursting disc(s) and manometer(s) to indicate disc rupture.

4.1.3.2.3 Vacuum Relief Valves

Vacuum relief valves are not recommended for use with TDI and MDI for various reasons. Most important is the risk of fouling / plugging of the vacuum valve by solids (there is no way to fit a bursting disc to prevent such fouling). A shell that is not to be fitted with a vacuum relief device shall be designed to withstand, without permanent deformation, an external pressure of not less than 0.4 bar above the internal pressure.

4.1.3.3 Transport Equipment Humidity Conditions

Fittings must be used through which dry air or nitrogen (dew point < -20 °C corresponding to approximately 1,020 ppm of water) can be applied to discharge the TDI or MDI. The pressurised dry air or nitrogen should be provided by the consignee.

Silica-gel filter:

The use of air produced by the compressor of the truck with or without the use of a silica-gel filter will provide wet air. It is strongly recommended not to use the compressor of the truck.

4.1.3.4 Thawing and Heating Systems

TDI and MDI are shipped in insulated tanks. Loading takes place normally at temperatures between 25°C and 45°C. Despite these precautions, there may be substantial heat loss before the tank reaches its final destination. If the temperature is less than 17 °C for TDI or less than 15 °C for MDI, the tank should be heated before it is unloaded. The product should be heated to 25 - 45 °C until all frozen product has thawed. Never allow the temperature to exceed 45°C as dimerisation may take place, potentially leading to off-spec product.

Remark:

Several product grades do require different temperature settings. For detailed information, you should consult with your supplier.

Freezing TDI will separate the isomers. Contact your supplier.

The best way to thaw frozen TDI and MDI is with water with a maximum temperature of 60°C. Hot water is less likely to cause dimerisation than steam. If hot water is not available, an alternative heat source is steam with a maximum absolute pressure of 1.7 bar (= 115 °C). Steam, if not watched very carefully, will overheat the TDI and MDI, causing dimerisation.

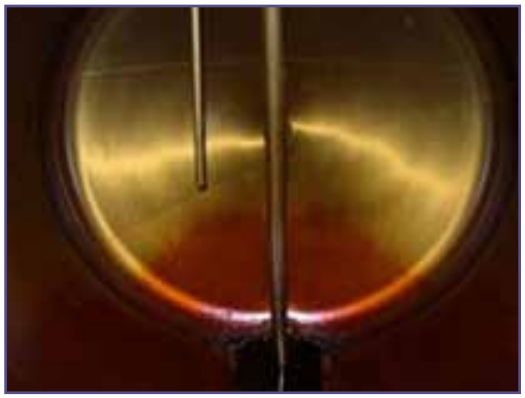
The heating coils should always be fitted externally and the temperature of the TDI and MDI inside must be monitored during heating.

An external electrical heating system can also be provided. It must be designed to maintain the contents of the tank within the temperature limits requested by the supplier of the TDI and MDI. The details cannot be stipulated in these Guidelines because the specification for such a system will depend on the product and grade to be carried. Thus, it is important that the supplier of the TDI and MDI and the carrier both fully understood the requirements for and the capabilities of the system.

For sensitive products, such as monomeric MDI, it is important that the electrical heating control system is capable of maintaining the shell at a controlled temperature when the tank is empty on the return journey.

The supply cable for electrical systems on isotanks and road tankers should terminate in a 5-pin plug (32 amp. 6h) or 4-pin plug (63 amp. 6h).

4.1.3.5 Sample Tubes



Sample tubes in tank containers and road tankers will not be accepted for loading at ISOPA Member Companies. If sampling is required by the customer, the responsibility for this operation is with the customer and a proper sample point in the discharge line of the customer should be used.

5 Safety Auditing of Road Carriers and Tank Operators

5.1 Carrier Capability: Assessment and Control

All ISOPA Member Companies use the services of professional road carriers to distribute their products. It is of vital importance that the chemical company is assured that the carriers being employed are competent and operating to appropriate safety standards. Customers undertaking their own TDI and MDI transportation should act in the same way.

The primary carrier is responsible for all its sub-contractors with respect to driver training and safety standards as defined in this Guideline.

5.2 Safety and Quality Assessment System

It is essential that suppliers periodically assure themselves as to the operational acceptability of the carriers. This can be done by auditing, e.g. using Cefic's Safety and Quality Assessment System (SQAS) for Road Haulage.

5.3 Meeting Safety and Regulatory Standards

Auditing does not replace or diminish the basic responsibility of the carrier to ensure that his equipment meets the appropriate safety and regulatory standards and is properly maintained.

6 Training for Drivers

6.1 Specific Requirements for TDI and MDI

In addition to legal requirements, drivers should be trained either by the consignors or the carriers to understand the specific dangers that can arise during the transport of TDI and / or MDI and the actions to be taken in an emergency.

All consignors should agree with carriers to include a requirement that all drivers conveying TDI and/or MDI have received training as specified in the ISOPA Driver Training program (www.isopa.org / logistics ehs / driver training).

6.2 General Product Information

The essential product information is given in Chapter 2. For more details see the producers' safety data sheets. From a driver's point of view, the essential points to note are:

- TDI is a liquid, but can easily solidify below 17°C
- For MDI, there are liquid polymeric as well as solid monomeric physical forms
- The vapour pressure of TDI is approx 20 times higher than MDI, leading to concentrations higher than the permissible workplace exposure limits at ambient temperatures.

Both TDI and MDI:

- Have vapours 6 times heavier than air
- Do not mix with, and are heavier than water
- Have high flash points (not classified as flammable liquid)
- Have an odour, but the level at which both products can be detected by smell is significantly higher than the permissible workplace exposure limits

6.3 Loading / Transport / Unloading Recommendations

The TDI / MDI producers have agreed on several recommendations and procedures to assure safe loading, transport and unloading of bulk products.

Procedures for the inspection of bulk transport equipment are given in Section 7.5. To assure safe transport of the products, recommendations are made in Chapter 8.

For bulk unloading the producers insist that there should be a well-defined division of responsibilities between the driver and the customer's personnel. The producers realise that procedures may vary, but Section 9.6 is a recommendation which is strongly advised to be adopted.

If a driver is concerned that the unloading procedure may not be completed in a safe working manner, then he should refuse to commence the discharge procedure and contact his management for advice.

6.4 Technical Proficiency

The driver is fully familiar with all the fittings and equipment associated with the tanker or tank containers, specifically with:

- The layout and operation of all the connections to the tank, including the operation of the dry gas supply system installed to prevent the ingress of moist air during unloading
- The heating system in order to maintain the product within the temperature limits specified by the supplier or customer

6.5 Spillages

In considering the various aspects of spillage, it is necessary to distinguish between minor spillages and major spillages involving, for example, a bulk road tanker. The most important criterion for distinguishing between the two is the ability of the people to deal with the occurrence on the spot. Hence, a minor spillage is defined as one which can be dealt with using existing equipment, while for a major spillage it would be necessary to summon outside assistance from the emergency services.

Spillage of a large quantity of a TDI / MDI should, as far as possible, be pumped into a suitable tank or packaging prior to its disposal.

If it is necessary to neutralise TDI / MDI, it should be done very carefully as the heat generated will increase the vapour hazard. See for details below and the formulations described in section 6.6.

6.5.1 Minor Spillages

- Clear the area of all non-essential people
- Inform the supervisor of the operation
- Put on respiratory protection in addition to the Personal Protective Equipment described in Sections 3.1 and 3.2
- Prevent further spillage if possible, **but without taking any personal risks**
- Cover the spillage with absorbent materials such as sand, wet earth or clay
- Pour liquid decontaminant (see Section 6.6) over the spillage and allow the mix to react for at least 30 minutes
- Shovel the absorbent and spilled material carefully in suitable open waste container(s) and add further amounts of liquid decontaminant
- Remove containers to a safe place and cover them loosely. After some days the residues may be set aside for disposal, preferably by incineration
- Wash down the contaminated area with large amounts of water or liquid decontaminant
- When safe conditions have been re-established, remove and decontaminate the protective equipment and return it to the place where it is normally kept

6.5.2 Major Spillages

In addition to the listed items under 6.5.1 the following items are important when dealing with major spillages.

- Keep up-wind to avoid inhalation of vapour
- Prevent access
- Notify emergency services immediately *
- The use of a self-contained breathing apparatus by the emergency team members is strongly recommended.

*** In the event of an accident in transit, notify the emergency services and the supplier immediately.**

- Contain and cover the spillage with fire-fighting foam (if not available, absorbent materials such as wet sand, wet earth or clay may be used). Care should be taken with organic absorbents such as sawdust, as in extreme cases it may start to burn as a result of the heat evolved from the neutralisation process. If possible, prevent the TDI / MDI from entering the drains. If TDI / MDI does enter the drains, inform the fire service and the water authority immediately.
- When absorbed (after around 15 minutes) shovel the absorbent and spilled material in suitable waste container(s) and add further amounts of liquid decontaminant. Quick removal will reduce further evaporation. Suitable containers are small sized open top drums (20-60 litre). However, other open top containers could be used as well. Drums should only be filled for about 70% and drums should be lightly covered TO AVOID POSSIBLE PRESSURE BUILD-UP. The container should be checked periodically for several days for subsequent disposal, preferably by incineration.

6.6 Liquid Decontaminant Solutions

Formulation (weight or volume)	*%*
Sodium carbonate	5 - 10
Liquid detergent	0.2 - 2
Water	to make up to 100%

The formulation above should normally be used for the neutralisation of spillages and decontamination of affected areas. Packaging and other materials used (e.g. tools) should also be decontaminated.

When using this formulation it should be added slowly and carefully to the TDI / MDI. This becomes more and more critical the larger the amount of TDI / MDI to be neutralised. This precaution is necessary because the reaction may generate heat resulting in an increased evolution of TDI / MDI vapour and the formation of carbon dioxide.

At temperatures below 0 °C an alcohol such as ethanol (industrial spirit), isopropanol or butanol can be added to the formulation to prevent the neutralizer from freezing. However, the use of alcohols means the decontaminant solution will become flammable, which increases the fire risk.

6.7 Fire

- Clear the area of all non-essential people
- Keep up-wind to avoid inhalation of vapour
- Prevent access
- Notify emergency services immediately *
- Inform the supervisor of the operation.

Any TDI / MDI involved in a fire may generate toxic fumes in concentrations harmful to health. Full protective equipment should be worn by all persons fighting the fire. It is crucial that self-contained breathing apparatus be used.

Suitable extinguishing agents include:

- Dry powder
- Carbon dioxide
- Protein-based foam
- Water *

*** If water is used, it must be in very large quantities. Care must be taken as the reaction between water and hot TDI / MDI may be vigorous.**

6.8 Emergency Response

All carriers involved in the transport of TDI and / or MDI must have a 24/7 emergency response system for receiving transport emergency messages and communicating with the local authorities and their suppliers. Carriers should have the capability to intervene with staff and logistic equipment in the event of an incident. Drivers should be trained as a first responder and how to alert the company and the emergency services.

All ISOPA Member Companies involved in the transport of TDI and / or MDI in Europe have a 24/7 emergency response system for receiving transport emergency messages from carriers, customers, emergency services and other stakeholders and for providing expert advice to minimise any hazard arising from an incident. An emergency response manual has been developed for TDI / MDI, which is available from the ISOPA website (www.isopa.org / emergency response).

The TDI and MDI producers have also established a Europe-wide emergency response / mutual aid scheme. The essentials of this scheme are given in Chapter 11.

7 Loading Operations

7.1 Compliance with Modal Transport Regulations

It is the responsibility of the loading point operator to ensure compliance with modal transport regulations relating to minimum / maximum ullage levels, if applicable, and with national and international weight limit regulations appropriate to the transport route to be followed.

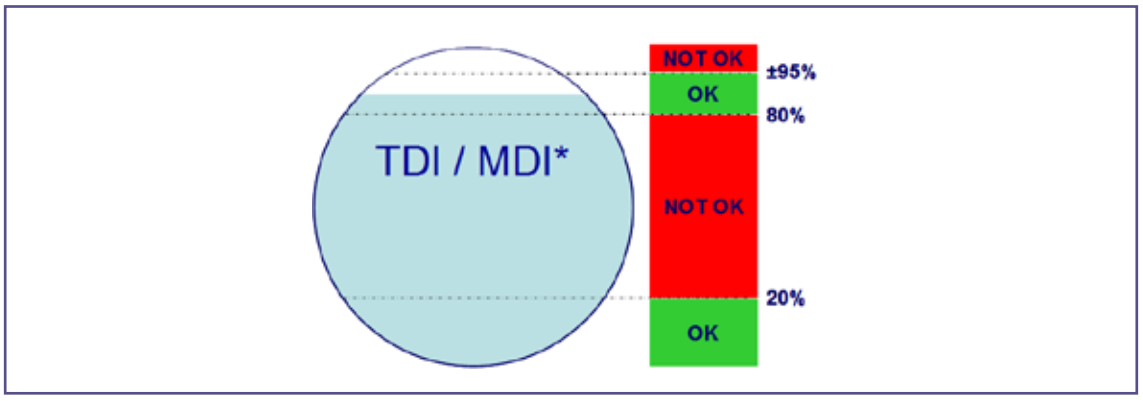
7.2 Availability of Written Operating Instructions

Written operating instructions should be available at all filling points covering the loading of TDI and MDI into bulk road tankers, isotanks and swap-body containers. Persons involved should be fully trained in their implementation. The instructions should address the specific hazards of the TDI / MDI concerned, and ensure the correct operation of filling equipment in both normal operations and in any emergency. Drivers should also be familiar with safety procedures, including site alarms and the use of safety equipment at the loading point.

7.3 80/20 rule

Under ADR Chapter 4.3.2.2.4, it is required that:

"Shells intended for the carriage of substances in the liquid state or liquefied gases or refrigerated liquefied gases, which are not divided by partitions or surge plates into sections of not more than 7500 litres capacity, shall be filled to not less than 80% or not more than 20% of their capacity."



*) This rule applies to dangerous goods only. Thus, the rule is valid for TDI but not for MDI because the latter is not classified as a dangerous substance according to ADR.

The purpose of the "80/20 rule" is to reduce the sloshing effect of the liquid inside the tank, which is particularly significant in partially loaded vehicles and impairs the vehicle stability and which does not depend on the hazardousness of the product.

Thus, it is strongly recommended to also apply this rule to any tank vehicles transporting MDI.

It is recommended that suppliers and carriers have appropriate controls in place to ensure that the "80/20 rule" is followed when planning TDI and MDI deliveries.

7.4 Loading TDI or MDI with Polyol in Adjacent Compartments

Based on ADR 4.3.2.3.6 it is not allowed to transport TDI and Polyol (formulated) in adjacent compartments unless these compartments are separated by a partition with a wall thickness equal to or greater than that of the tank itself. They may also be carried separated by an empty space or an empty compartment between loaded compartments.

Based on the above it is strongly advised to follow the same procedure for MDI. Although not regulated, MDI has the same reactivity characteristics as TDI.

7.5 Inspection of Bulk Transport Equipment

As part of the operating instructions, an inspection of the bulk transport equipment should be carried out by the loading terminal staff before, during, and after loading. This inspection does not replace or diminish the responsibility of the operator of bulk transport equipment to ensure that it is properly tested, maintained, fit-for-purpose and ready for loading. It is meant to ensure that the transport of TDI and MDI is conducted as safely as possible. The inspection list detailed in Section 7.5.1 is recommended for use by the loader when checking the condition of the TDI and MDI bulk transport equipment, and should be applied for all filling operations.

The inspection list assumes that TDI and MDI are to be conveyed by international transport. In circumstances where TDI and MDI are to be conveyed nationally in accordance with regulations which may differ from the requirements laid down in international transport agreements, the inspection list should be modified accordingly.

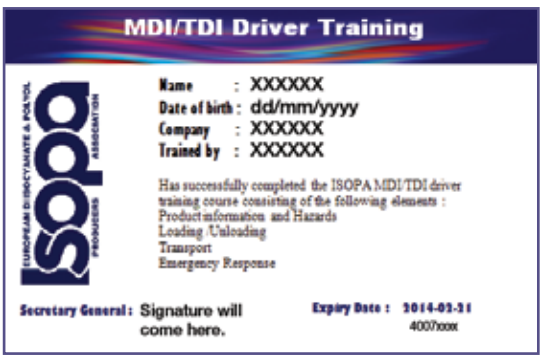
In addition to the routine inspection of all bulk transport equipment prior to each loading operation, a responsible person from the loading company should carry out a check on each road tanker or isotank prior to its initial introduction, or reintroduction, into service after maintenance or repair. These checks are also shown in detail in Section 8.10.

7.5.1 Routine Inspection of Road Tankers and Tank Containers at Loading Terminals

If any of the following conditions are not met, the loading operation should be stopped and the situation rectified before loading is allowed to continue:

Administration procedures

1. Has the driver a valid ADR certificate (only for TDI) for the transport of dangerous goods?
2. In addition, has the driver a valid TDI / MDI* Driver Training certificate?
3. Check that the vehicle capacity is adequate for the quantity to be loaded and that, when loaded, ullage and maximum allowed gross vehicle weight, which can differ per country, will be within regulatory limits.



*** MDI has been declassified by the UN Committee of Experts as described under 1.2. Nevertheless, for reasons of Responsible Care®, the design of bulk transport units carrying MDI should remain the same as before the declassification of MDI.**

Before loading

1. Are there any visual defects on the truck which could constitute a hazard? (for example defective lights, tyres....).
2. Were all valves, domes and manholes closed upon arrival?
3. Tank inspection for cleanliness, if practised by the supplier, must be undertaken at this point. Driver must present a certificate of cleanliness and a dew point certificate (-20 °C) or a declaration that the previous cargo was also TDI or MDI.
4. Only for TDI: Are all "dangerous goods" labels and the orange-coloured Kemler plate (60/2078) fitted? Are the Instructions in writing - in the required language(s) - on board?
5. Only for TDI: The class number (6) should appear in the bottom corner of the label for class 6.1 (toxic).
6. Does the driver have all the necessary items of protective clothing and safety equipment? (for further details see Chapter 3).
7. Have the correct caps or blind flanges been fitted with all the necessary bolts and gaskets in place?
8. Does the vehicle have all the necessary specific equipment and is it clean and in proper working order?
   a. ADR standard equipment
   b. Air-drier, compressor, insulation, heating device, safety relief valve, vapour return connection and sampling valve, if required
9. Do all valves function correctly (freedom of movement) and are they fully closed?
10. Notify the supervisor of operations at the loading point of the quantity to be loaded.

Whilst loading

1. Continuous monitoring of the loading operation is essential.
2. Ensure that the maximum and the minimum permissible filling levels are not exceeded.

After loading

1. Check that the maximum permitted gross vehicle weight has not been exceeded.
2. Are all the valves closed and the blind flanges fitted, with all gaskets and bolts in place?
3. Are all the domes closed?
4. Verify the external cleanliness and the absence of overflow.
5. Verify the cleanliness of the spillage trays.

7.5.2 Initial Inspection of Road Tankers, Tank Containers & Swap-body Containers

First introduction

Before road tankers, tank containers and swap-body containers are first introduced to TDI / MDI service, a responsible person from the loading company should carry out a check on the following items:

1. Has the tank been properly cleaned? (availability of certificate of cleanliness).
2. Check that measures have been taken to ensure that the compartment atmosphere has a dew point of < -20 °C.
3. Continue with appropriate routine inspection as stated in 7.5.

Reintroduction to service

See Section 8.10.

7.5.3 Maintenance of Transport Equipment

During operations, unscheduled maintenance of the transport equipment may be necessary, for example, if polymers formed by the reaction of TDI / MDI with (atmospheric) humidity are choking valves and piping.

Customers should be instructed to report immediately to the consignor any difficulties which are experienced. The provision of an information tag on the returning transport equipment identifying the difficulty can be of assistance.

8 Road and Intermodal Transport

8.1 Carrier Responsibilities

The carrier is responsible for the safe transport of TDI / MDI by road from the loading point to the unloading point. The following should be complied with:

8.2 Instructions in Writing - only for TDI

As an aid during an accident emergency situation that may occur or arise during carriage, instructions in writing in the form specified in Section 5.4.3.4 of ADR shall be carried in the vehicle crew's cab and shall be readily available.

These instructions shall be provided by the carrier to the vehicle crew in the languages that each member can read and understand before the commencement of the journey. The carrier shall ensure that each member of the vehicle crew understands and is capable of properly carrying out the instructions.

Before the start of the journey, the members of the vehicle crew shall inform themselves of the dangerous goods loaded and consult the instructions in writing for details on actions to be taken in the event of an accident or emergency.

8.3 Routing

The route to be followed must be selected carefully by the carrier and should be given, on request, to the consignor. However, compliance with bridge, tunnel or local routing regulations or restrictions is entirely the responsibility of the carrier. As with all hazardous chemicals, as far as possible, the route should:

- Follow motorways
- Avoid areas of high population density

8.4 Safe Parking

Drivers of vehicles conveying TDI or MDI must, whilst on the road, ensure that the vehicle, when not being driven, is either supervised at all times or is parked in a safe place. Particular attention is needed when selecting a safe parking location. A secure depot or secure factory premises should be used whenever possible. Preferably, parking should be in an isolated position in the open, in an area which is lit at night. It is strongly recommended that receivers provide secure parking for vehicles which have arrived outside specific access times.

8.5 Severe Weather Conditions

As with all hazardous chemicals, when severe weather conditions are experienced during the transport of TDI or MDI, for example, icy roads, snow or poor visibility, the vehicle must stop at the next suitable parking place. The vehicle should not continue with the delivery until the weather conditions improve.

In some European countries this is mandatory for all hazardous materials.

8.6 Delays or Accidents

All delays during transport, whether caused by severe weather conditions, breakdown or any other reason must be reported to the consignor as soon as possible.

In the event of an accident during the journey involving the immobilisation of the vehicle, or product spillage, or potential loss of containment, the driver and carrier must follow the company's emergency response procedure and, in case of TDI, the instructions in writing (see 8.2). Details of the accident should be reported to the consignor / supplying company as a matter of urgency. Remote expert advice can be provided through the supplier's emergency number and in case emergency assistance on the scene of the incident is required the ISOPA's Emergency Response Scheme (see Chapter 11) may be activated.

8.7 Temperature Checks during the Journey

During the bulk transport of TDI / MDI, the temperature of the tank contents should be checked regularly and recorded on a checklist or in a logbook.

If the temperature of the tank contents should rise more than 5 °C above that specified by the supplier, the driver should immediately alert his company, who should subsequently inform the supplier to seek instructions.

As a minimum, the temperature of the product should be checked immediately after loading and prior to unloading.

8.8 Multi-Modal Movements

For multi-modal carriage that is not driver / tractor accompanied during the rail-sea stage, particular attention must be given to ensure that the road vehicle used for the final delivery is properly labelled with the appropriate placards and - only for TDI - carries appropriate instructions in writing as specified in Section 8.2. Responsibility lies with the transport company.

The consignor should consider carrying out a safety assessment at the container terminals handling the transfer between the modes of transport. The assessment should give particular consideration to the storage facilities for hazardous materials (e.g. segregation) and available emergency equipment.

8.9 Opening Tank Containers

Sample taking from tank containers should be avoided. Accordingly, a special sticker must be attached to the manlid to discourage the opening of manlids.

ISOPA has made a supporting letter available for drivers to discourage customs authorities opening tank containers for inspection. This document is available on the ISOPA website (www.isopa.org).

8.10 Reintroduction of Equipment to Service

Before road tankers, tank containers, or swap-body containers are reintroduced to service following maintenance or repair, an authorised person from the owner of the equipment or his appointed contractor should carry out a check on the following items:

1. Check that maintenance and repairs have been carried out effectively and compare them with the work requested.
2. Has the tank been properly cleaned? (availability of certificate of cleanliness).
3. Check that measures have been taken to ensure that the compartment atmosphere has a dew point of < -20 °C.
4. Are all openings closed and are all bolts present and correctly tightened?

9 Unloading Operations

Responsibilities according to BBS-Guidelines:

The roles and responsibilities in loading and unloading operations as agreed between CEFIC and ECTA are described in the CEFIC-ECTA:

"Behaviour Based Safety Guidelines for the Safe Loading and Unloading of Road Freight Vehicles" (Issue 2 March 2007).

9.1 Responsibilities According to the Provisions of the "Seveso Directive"

The Directive on the Major Accident Hazards of Certain Industrial Activities (82/501/EEC) which was adopted in 1982, and updated in 1996 (96/82/EC) is generally known as the "Seveso Directive", provided the members of the European Community with uniform rules for:

1. The prevention of major industrial accidents or limitation of damage in the event of an accident, and
2. The avoidance of environmental damage

This Council Directive in its currently valid version is of importance to all members of the polyurethane industry who process and store TDI in quantities above defined limit which is currently 10 ton and restricted to a maximum of 100 ton. The Directive only applies to EU member states, but could be superseded by national legislation. Non Member States could also decide to implement the EU-Directive.

In all cases the management of the plant must take measures and be able at any time to provide evidence to the authorities, if requested, that they have:

- Identified the major accident hazards
- Adopted suitable safety measures, and
- Provided persons working on the site with safety information, training and the appropriate equipment:
  - to prevent major accidents (i.e. spillages and emissions during unloading)
  - to take appropriate measures in the event of an accident, and
  - to limit the consequences for humans and the environment if accidents occur

For further information on meeting the requirements of the "Seveso Directive", see ISOPA's **"Guidance on the Seveso Directive and its Application to Polyurethane Manufacturers".**

9.2 Criteria for Discharge Facilities

The TDI / MDI discharging operation is potentially hazardous. Consideration must be given to the potential hazards associated with TDI and MDI, so it is important that discharge facilities are:

- suitably located,
- correctly designed and constructed,
- properly used and maintained and
- regularly checked for the maintenance of the standards set (see Safety Assessment)

9.3 Safety Assessment for Unloading and Storage Facilities

The conditions for the reception of deliveries of TDI / MDI at a customer's premises are the customer's responsibility. It is recommended that suppliers, at the customer's request and in cooperation with the customer, arrange a safety assessment of the customer's unloading and storage facilities prior to an initial delivery and at intervals thereafter, in accordance with the ISOPA assessment checklist.

The ISOPA assessment scheme serves to support users of isocyanates to evaluate their bulk unloading facilities and the checklist can be downloaded from www.isopa.org. The objective is to ensure that good safety standards are maintained during product handling and storage and to share best practices in the industry. ISOPA Member Companies make regular updates to the assessment checklist.

9.4 Criteria for Discharge Hoses

It is strongly recommended that customers should own all discharge hoses and vapour return hoses required for product discharge, that these be specifically selected for TDI / MDI service and be fitted with a ball valve at the tanker-connection end, or equipped with an equivalent means of sealing the hose (e.g. blind flange).

Product loading and unloading hoses / lines should be DN50. The vapour return hose / line should have a sufficient diameter proportionate to the pump capacity and should be connected to the DN50 vapour return connection.

9.5 Operator Protective Equipment

All necessary protective clothing and emergency equipment should be available for discharging operations (for further details, see Chapter 3). Persons should be trained in the correct use of this clothing and equipment. Whenever the driver leaves his vehicle, he should wear the minimum required personal protective equipment to ensure his personal safety in the event of an emergency.

9.6 Recommended Procedures for Unloading of Bulk Equipment

Bulk discharge should preferably be carried out by means of pumps rather than pressurized air or nitrogen. Road tankers and tank containers are equipped for top unloading only, so the discharge is via a dip pipe. Use of a vapour return system is highly recommended not only for safety reasons (preventing release of TDI / MDI vapours and vacuum damage) but also from a product quality perspective.

If a pump is used for product discharge it is preferable to use a sealless type (e.g. magnetic driven pump). However, mechanical seal pumps are also acceptable. If a positive displacement pump is used it should be fitted with a pressure relief valve with the discharge on the suction side of the pump.

The discharge facility must be constructed adequately in order to prevent vacuum conditions in the vehicle tank.

Written operating procedures covering all aspects of the discharge of TDI / MDI must be prepared by the owner of the discharge facility. Specific procedures concerning the division of responsibilities between the driver and the cargo receiver are required.

Due to variations in the configuration of cargo reception facilities, the following recommended procedure must not be taken as an absolute guide to the activities involved or the sequence in which they are conducted. The purpose of this section is to demonstrate the complexity of the operation and the consequent need for clear agreement on the division of responsibility between those involved.

The driver has a duty to his employer to protect the integrity of the vehicle. The receiver has a duty to ensure that product is discharged into the correct tank in such a way as to preserve the quality of the product. Both must cooperate fully in the discharge process to ensure that it is transferred safely!

RECOMMENDED PROCEDURES FOR UNLOADING OF ROADTANKERS / TANKCONTAINERS

Receiver's operator	*Driver*
	1. Drives to the reception area
	2. Hands over all relevant documents to the operator. Documents may include: weighing ticket, delivery note, certificate of analysis and transport document. Shows his ISOPA TDI / MDI driver training certificate.
3. Checks that: the same product name appears on: - the unloading point - the unloading permit - the waybill / transport document - the certificate of analysis the same tank / isotank registration number appears on: - the unloading permit - the waybill / transport document the driver has a valid ISOPA TDI / MDI driver training certificate.	

Receiver's operator	*Driver*
4. Only for TDI: Checks that the orange-coloured Kemler plate and the waybill are identical to: - those of the unloading point - those of the unloading permit	
5. Checks the weight to be unloaded on the unloading permit. Makes sure that the reception tank can accommodate the load.	
6. Directs the tanker to the unloading point and remains at the unloading location for the duration of the operation.	
	7. Positions his vehicle, as far as possible, ready for emergency evacuation.
8. Ensures wheels are blocked with two (2) chocks.	8. Prepares vehicle for unloading: - shuts off the engine - applies the handbrake
9. Installs signs in front and behind the tanker indicating that a product transfer is taking place.	
10. The receiver and the driver put on their individual protective equipment.	
11. Tells the driver where to find: - the safety shower and eyewash - the fire extinguisher - the emergency stop button - the telephone or intercom and briefs the driver on site emergency procedures	
12. In case of disagreement, the receiver or driver: - refuses to unload - informs the site road traffic office and the carrier's planner - each consults his superior for instructions - notes the incident in the events register	
13. Installs the gangway providing safe access to the top of the vehicle. Alternatively, prepares the fall arrest system for use.	
14. The driver opens the lid of the spillage tray of the vehicle.	
	15. Ensures that all vehicle valves are fully closed. Removes blind flanges or caps from all outlets.
16. Checks that site equipment – e.g. product hose, vapour return or nitrogen/air pressure line, couplings, gaskets and seals – is in good condition, fit for purpose and carry out a visual check on the internal cleanliness.	16. Carries out a visual check on the **cleanliness** and correct functioning of the vehicle valves.

Receiver's operator	*Driver*
17. FOR PUMP DISCHARGE ONLY:	
17a. With a vapour return line	
a. Installs the vapour return line connection to the storage tank. b. Ensures valves on the vapour return line are open. c. Ensures the pump versus vapour flow capacity is such that the pressure in the transport tank is never below atmospheric conditions.	d. Installs the vapour return line connection to the vehicle e. Ensures valves on the vapour line are open.
17b. If no vapour return line exists	
a. Ensures the dry air flow capacity is such that the pressure in the transport tank is never below atmospheric conditions.	b. Connects and opens the tanker air vent to the receiver's dry air / nitrogen supply
18. FOR PRESSURE DISCHARGE ONLY:	
a. Ensures the dry gas supply is free of impurities, especially water, rust, etc. b. Ensures the dry air pressure does not exceed two (2) bar.	c. to connect the dry air / nitrogen (for MDI monomer nitrogen is preferred) to the vehicle.
19. a Checks the presence and state of the couplings and gaskets and connects the unloading arm or flexible hose.	19. b Assists the receiver.
20. If the product conforms to its specification, starts the unloading procedure.	
21. a) Opens the hose or unloading arm valve.	21. b) Checks the receiver's actions.
22. Takes a sample, if required, but only from the fixed discharge line or the storage tank.	
23. TOP DISCHARGE BY PUMP:	
a. Opens the valve on the receiver's line.	b. Opens the tanker outlet valve.
24. TOP DISCHARGE BY PRESSURE:	
a. Opens the dry gas supply valve. c. Opens the valve on the receiver's line when pressure has built up in the tanker.	b. Opens the vehicle dry gas inlet valve. d. Opens the tanker outlet valve.
25. a) Observes and controls the transfer including the product level in the reception tank. If any anomaly linked to product discharge is detected, the receiver must: - immediately stop the discharge - inform management and seek instructions - record the incident in the register of events	25. b) Attends the vehicle during transfer to observe and assist in any emergency.

Receiver's operator	*Driver*
At the End of the Transfer Operation:	
26. TOP DISCHARGE BY PUMP:	
a. Manipulates the hose to provide gravity flow to the pump enhancing hose drainage. b. Closes the valve on the receiver's line. c. Stops the pump.	
27. TOP DISCHARGE BY PRESSURE:	
a. Closes the dry gas supply valve. b. Disconnects the dry gas supply line. c. Allows the tanker to decompress via the receiver's cargo line to a maximum of 0.1 bar. d. Closes the valve on the receiver's line.	e. Shuts off the tanker connections.
Always check if the transport tank and/or equipment is under pressure before making or breaking any connections.	
28. a) Disconnects the unloading arm or flexible hose and drains the residue into a safe container; these items should then be capped and stowed away safely in a dry place.	28. b) Assists the receiver.
	29. Refits the caps / blind flanges on the vehicle connections.
30. Withdraws the gangway and locks it in the upper position or stows away the fall arrest system.	
31. The receiver and the driver remove their individual protective equipment, carefully checking if any item was contaminated during the discharge process.	
32. a) Authorizes the driver to leave the unloading area.	32. b) The driver should ensure that it is safe to leave the (un)loading area by walking around the vehicle and perform a 3-Minutes check after discharge. **Equipment:** - Disconnected? - Free of spillages including spillage tray? - Safety handrail down? - Valves closed and blind-flanged, manlids closed? - Spillage tray covers closed? - Only slight overpressure (max 0.1 bar)? - Depressurise at the customer if possible, or inform planner **Documentation:** - Transport documentation signed?

Receiver's operator	*Driver*
33. Both leave the discharge area.	
34. Measures the product level in the reception tank. Closes all reception circuits.	

9.7 Non-Standard Operations (NSO)

A "standard" delivery to customer site for TDI and MDI is characterised as follows:

- Agreed carrier, loading and delivery dates, product volume and loading location.
- Carrier equipment fits the order (see also Section 7.3 on the 80/20 rule).
- Appropriate shipping documents are present and no additional product handling during loading, transit or unloading (e.g. no local ad-hoc filtering or trans-loading into other truck / equipment).
- Discharge fully at a known customer unloading location without return product.
- No disruptions after the discharge has started.

An operation that is different from the definition of "standard" described above is "non standard". Suppliers and carriers should proactively monitor for these Non Standard Operations (NSO) and make sure to evaluate the operational risks. NSO increase the likelihood of errors and incidents and could place drivers, operators or the environment at risk. Thus, it is recommended that a structural analysis is done to either eliminate any NSO or to manage the risk at acceptable levels.

Given the non-specific nature of NSO, it is not possible to make an extensive NSO list. However, three regularly occurring NSO have been identified with suggested control mechanisms as listed below. Carriers are encouraged to report NSO and / or potentially unsafe situations to the supplying ISOPA Member Company. If a driver is in doubt whether the unloading operation can be done safely, he should not commence discharging at all and contact his planning department who can subsequently ask support from the supplier.

9.7.1 Direct Discharge from Bulk Equipment into IBC or Drums

The potential health, safety and environmental risks involved in unloading from bulk equipment directly into drums or Intermediate Bulk Containers (IBCs) without using a fixed installation are:

- Loss of containment of product resulting from leakage, human error, malfunction of equipment or overfilling.
- Human exposure and a potential for serious injury.
- In the case of flammable products, there are known cases where fire or explosion during this operation led to multiple fatalities and/or major asset damage to customer facilities or logistics equipment.

For the reasons mentioned above it is strongly recommended not to directly unload from the bulk equipment with a hose into a drum or IBC. To unload into drums or IBCs safely, a fixed filling installation must be available.

"Fixed" means that an installation is equipped with a fixed discharge connection. The driver and customer operator can connect the hose directly to the manifold of the filling installation and the truck can be discharged without interruption (essentially, no different in operation compared to discharge to a storage tank). Obviously the product should always be handled in accordance with the Safety Data Sheet requirements (e.g. use appropriate Personal Protective Equipment).

The requirements for a fixed installation are:

	Requirements Drum / IBC filling installation	*MDI*	*TDI*
1	The filling process is monitored and avoids product overfill and spill. Secondary containment available	X	X
2	Driver is **not** involved in actual drum or IBC filling operation	X	X
3	A fume collection system removes vapours during filling of drums / IBCs		X

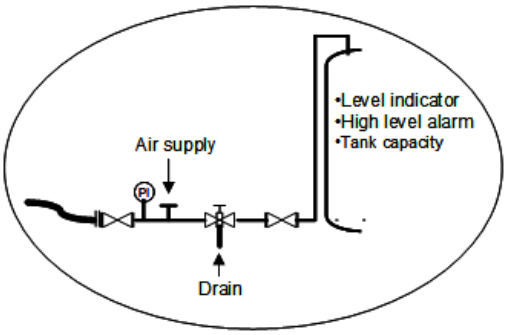
The driver is not in charge of assessing a fixed drum / IBC installation!

If the driver can connect to a fixed installation at the customer site without any additional actions by himself compared to a normal discharge into a storage tank, he should only mention this situation to his planner who subsequently informs the supplier. If the intention is to directly discharge into IBCs from the tanker without a fixed installation, he should not start and contact his planning department who will get support from the supplier.

9.7.2 Unloading into more than one Storage Tank or incomplete Unloading

Discharge into more than one storage tank is allowed if the unloading hose is connected to a single manifold leading to multiple storage tanks and the hose is not disconnected during the unloading operation.

For those situations where delivery goes into more than one storage tank and the discharge hose must be disconnected during unloading, the hose or customer's installation should be equipped with a device to safely empty the contents of the hose after the first discharge. This can be done by means of an adaptor fitted with an air valve between the unloading hose and the customer's inlet connection similar to that illustrated below. Note how the adaptor allows the hose to be flushed back into the tank container before it is connected to the next storage tank. This operation should be carried out by the customer with properly trained operators and technical equipment without exposing the driver to any risks.



9.7.3 Insufficient Capacity of Storage Tank

The driver should proactively ask the customer to confirm that there is sufficient ullage in the receiving storage tank and only start the discharge if the answer is positive. If for any reason the discharge cannot be completed then the truck driver should wait until there is enough space in the receiving customer's tank to resume the discharge operation safely. If this is not possible within a realistic timeframe and the truck cannot be completely unloaded, this should be recorded in the remark field of the transport document and the supplier should be informed accordingly. Ideally, disconnection of the hose should be done as described in 9.7.2 and the incident should be recorded by the parties involved. Any partially loaded vehicles embarking on a return trip to the supplier should comply with the "80/20 rule" (see Section 7.3)

10. Storage Operations

It is not the intention of these guidelines to provide detailed engineering advice on the design of TDI / MDI storage facilities. Storage facilities should comply with all regulatory requirements and expert engineering advice should be sought for the design of such facilities. The main requirements of such storage facilities are described below.

10.1 Tank Size

TDI / MDI storage tanks should have sufficient capacity to store a full truck load (25 MT). If the volume is divided over multiple tanks, it is recommended that there is a single manifold at the discharge area of the tanks (see also Section 9.7 on Non-Standard Operations)

10.2 Bunding

A tank bunding with a capacity of 110% of the largest tank should be available. The bund floor and walls should be impervious and have no cracks. Any draining valves in the bund should normally remain closed. TDI / MDI tanks should not be placed in the same bund with different products (e.g. polyols).

10.3 Inlet Gas

Preferably, the inlet gas should be dry because TDI / MDI is hygroscopic (e.g. dry air or nitrogen). If air is used as the inlet gas, it should have a dew point of –20°C.

10.4 Venting

Any storage tank vents should lead to a safe place outside the storage building, preferably through a scrubber. Suitable scrubbing agents include polyglycols, (e.g. polypropylene glycol), polyols, decontaminant solution, etc. The vent lines of tanks containing different products should not be combined together in order to avoid cross contamination.

10.5 Level Indicator and Alarm

A reliable level indicator should be installed. Side level indicators are not recommended. The preferred types of level indicators are top mounted (e.g. radar, ultrasonic, magnetic, etc.). If a side level indicator is used, it should be of the magnetic type or be protected against external impact. Plastic tube level indicators should not be used. An independent high-level alarm that automatically stops the discharge pump is also highly recommended.

10.6 Pressure / Vacuum Protection

The storage tank should have appropriate pressure and vacuum control / protection to constantly maintain the designed safety pressure range. A visible pressure indicator should also be installed.

10.7 Temperature Control

The storage temperature should be automatically controlled either by controlling the storage building temperature or by means of a suitable electrical tracing or oil heating system. If a heating fluid is used, appropriate measures must be in place to ensure it cannot come into contact with the product.

10.8 Circulation

If the product will remain in the tank for a prolonged period, it is recommended that the option be available to recirculate the product by pump. Circulation is also advantageous when the product needs to be heated or cooled.

11 ISOPA's Mutual Aid Scheme for Providing Assistance at Transport / Unloading Emergencies

In many European countries, National Emergency Response Schemes for hazardous materials exist. Such schemes must take precedence over any advice given in this chapter. Furthermore, a Europe-wide Emergency Response System organised by CEFIC (International Chemical Environment = ICE) combining the national schemes and the schemes for special product groups is already established.

The information given hereafter concerns the ISOPA Emergency Response Programme which is integrated into ICE.

11.1 Purpose and Scope

The ISOPA programme is specifically designed for incidents involving the transport and unloading of TDI and MDI. It gives information on the particular characteristics of these products and provides training advice for personnel handling them.

Its radius of action covers all European countries, since the ability of an individual chemical company to provide expert advice quickly at the scene of an incident may be severely restricted if a considerable distance has to be travelled to reach the location.

With the objective of ensuring that expert assistance is available as promptly as possible at the scene of any TDI / MDI transport or unloading emergency, ISOPA Member Companies participate in a mutual aid scheme for emergency response.

11.2 Preparedness and Emergency Advice Requirements

All chemical companies involved in the transport of TDI / MDI in Europe have a system (24-hour manning) for receiving transport emergency messages and for providing expert advice to minimise any hazard arising from an incident. Additionally, they maintain a preparedness to attend the scene of the incident and to take, or assist in, remedial action to resolve the problem. In cases where the local or national Emergency Authorities are in control of the incident, the role of the company representatives at the scene would be to:

- Offer advice based on technical product knowledge to the Emergency Authorities and
- When agreed with, and requested by, the Emergency Authorities to organise the provision of spare vehicles / pumps / hoses / other equipment for cargo transfer, decontamination, etc., and to be prepared, on behalf of the Emergency Authorities, to employ their technical expertise in the conduct or supervision of remedial action to render the incident safe

11.3 Contractual Liabilities

The ISOPA Member Companies have signed "*The Convention for Providing Mutual Aid in the Case of Incidents during the Transport (and Unloading) of TDI and MDI*" including but not limited to the following principles:

- The Company which has supplied the MDI / TDI (the Requesting Company) has the general obligation to respond to the emergency
- A second Company (*the Assisting Company*) may also be asked by the Requesting Company to respond, in order to provide:
  - a quicker response, if the Assisting Company is closer to the scene of the incident
  - equipment
  - trained personnel
- The *Requesting Company* retains the responsibility for providing emergency assistance to the Authorities even though an Assisting Company may have been requested to participate
- The *Assisting Company* acts on behalf of the Requesting Company until the latter's representatives reach the scene
- All *Companies* participating in these arrangements will make available such services and assistance as would be provided for their own MDI / TDI

11.4 Technical Communication

Regular, at least annual, technical communications have been established between participating Companies in order to:

- Prepare and maintain an Emergency Response Manual based on the principles described in Section 10.3
- Ensure that the training and equipment at participating centres is adequate
- Agree on common methods of approach in the resolution of transport emergency situations

To facilitate the implementation of ISOPA's Mutual Aid Scheme in Europe, each ISOPA member company has been assigned the responsibility for a specific country or geographical area with a designated focal point manager with the necessary expertise. This focal point also functions as a contact for National Schemes and ICE (See ISOPA Guidelines "Emergency Response Manual for Transport of TDI and MDI").

11.5 Use of the Mutual Aid Scheme

The essentials of this scheme are as follows:

If, during the transport* of a shipment of TDI or MDI from Company A (its producer / consignor) to a customer, an incident occurs which Company A believes might cause damage to:

- people
- property
- the environment

or that the incident is such that it is unsafe to allow the shipment to continue,
then *Company A* can ask *Company B* (who is another TDI / MDI producer) to provide assistance in dealing with the incident on its behalf.

Drivers should follow the normal procedure in the event of any incident, that is, they or their principals should report the details to the emergency services immediately, and inform the consignor as a matter of urgency. It will be the decision of the consignor to request assistance from another company according to this scheme.

Under the ISOPA scheme, the company providing the assistance may send experts and equipment to deal with the incident. These experts are authorised to provide advice and assistance to the Emergency Authorities.

*** In this context transport means all the activities of the vehicle including unloading at the destination.**

APPENDIX 1:

Reaction of Diisocyanates with Water

Reaction of MDI and Water

When MDI is added to water, its R-N=C=O groups react readily with O-H groups of the water to form unstable carbonic acid (R-N-COOH) that dissociates as Carbon Dioxide gas (CO_2) and amines ($R\text{-}NH_2$).

The Amine ($R\text{-}NH_2$) then readily reacts with remaining MDI (R'-NCO) to produce inert, solid, insoluble polyurea (R-NH-CO-NH-R').

Every 250.26 grams of Monomeric MDI consumes 18 grams water and produces 25 litre CO_2 gas.

Reaction of TDI and Water

Toluene diisocyanates react with water and most acids to produce unstable carbonic acids, which subsequently decarboxylate (raising the pressure in closed containers) to yield relatively chemically inert and insoluble polymeric urea.

Toluene diisocyanates dimerize slowly at ambient temperatures and more rapidly at elevated temperatures.

Every 174 grams TDI consumes 18 grams water and produces 25 litre CO_2 gas.

Practical Meaning of this Reaction in the Supply Chain

- **Danger of free water in a container before loading**

  20 kg of water in MDI or TDI will create 20/18 * 44 = 49 kg CO_2

  = 27.25 m^3 at 25°C and 1 atmosphere pressure.

  In a 25 m^3 tank container with 20 m^3 TDI (80%) this is 5.45 bar extra.

- **Absorb the spill before neutralizing the isocyanate**

  The hydrolysis of isocyanates in aqueous solution is rapid. The subsequent reaction of the formed amine with further isocyanate producing urea is even faster.

  When isocyanates comes into contact with water, it does not disperse readily, but forms globules or solid masses reacting at their surface to form an impermeable inert polyurea crust separating the liquid isocyanate from the water.

  Thus, large spills of isocyanate in water do not react rapidly.

Sand or other absorbing materials will disperse the isocyanate and significantly increase the contact area when mixed with water after absorbing the spill. This is very advantageous in the rapid elimination of the danger.

Once the isocyanate has reacted with water the reaction product is not hazardous.

- **Collect contaminated PPE in bins and allow venting**

Note that the reaction also produces Carbon dioxide (gas) that will increase the pressure in a contained environment. For this reason, contaminated PPE needs to be collected in waste bins that are NOT to be tightened shut.

- **Keep the container dry and closed to avoid moisture ingress**

Moisture in the container will form polyurea which sticks to the wall of the container and is inert. This makes it difficult to clean other than with mechanical means. Polyurea will form flakes and grains that ultimately plugs the filter (or the nozzles).

Use of silica-gel filters between the compressor and the container is useless as compressed air will easily reach up to 70°C after about 10 minutes. This hot airflow over the silica-gel filter will effectively regenerate the silica-gel by absorbing all moisture previously adsorbed in the filter back into the airflow.

ONE voice

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EUROPEAN DIISOCYANATE & POLYOL
isopa
PRODUCERS ASSOCIATION

Contact

Avenue E. Van Nieuwenhuyse Laan 4
B-1160 Brussels
Belgium

Tel: +32 2 676 7475
Fax: +32 2 676 7479

www.isopa.org