www.isopa.org



FOURTH EDITION 2021

# GUIDELINES FOR SAFE LOADING/UNLOADING, TRANSPORTATION AND STORAGE OF TDI AND MDI IN BULK



# Foreword

The third revision of these Guidelines, dated March 2011, has been reviewed and updated by ISOPA's Logistics EHS Working Group.

The intention is to contribute to the overall safety standards in the supply of diisocyanates. In this version, you will find improvements to address learnings from incidents in the industry as well as changes suggested to the ISOPA Logistics Working Group during the recent carrier days.

The analysis of recent incidents discovered that a common root cause lies in the communication between operators and drivers. To reduce these issues, these Guidelines have been changed to give more clear directions on accountability on actions and communication between operators and drivers.

We want to thank J. Fietz for his contribution to this update.

- F. Burrekers, chair Shell
- F. Pieters BASF
- P. van Haarlem Dow
- D. Stefanovics Borsodchem
- R. Van der Kooij Huntsman
- O. Schopmeier Covestro
- T. Gross Covestro

# **Preface to the 4th Revision**

The main changes in this fourth revision are as follows:

#### Chapter 2:

- Paragraph 2.2 on REACH was added

#### Chapter 3:

- was updated with new pictures
- PPE's listed in table
- AP2 as minimum filter added
- Drivers should have eyewash bottle with them during isocyanate transport

#### Chapter 4:

- Paragraph 4.1.3.1 was updated with suggested materials for gaskets
- Paragraph 4.1.3.4 has been updated with temperature verification (during transport) against supplier specifications
- Paragraph 4.1.3.5 has a recommendation not to take samples nor to use accompanying samples with the shipment

#### Chapter 6:

- Paragraph 6.1 states that driver training should be provided in either the mother language of the driver or a language that they understand and speak
- Paragraph 6.3 has been updated to include the producer's view that the (un)loading party should have the leading role in the (un)loading process and not the driver
- Paragraph 6.4 has been updated to be aligned to changes in paragraph 6.3
- Paragraph 6.5 has been updated to be more clear

#### Chapter 7:

- Paragraph 7.2.1 is a new paragraph on the importance of language skills
- Paragraph 7.5 was extended with a checklist for tank container inspections

#### Chapter 9:

- The first line of the chapter was updated with text from the updated CEFIC best practice on (un)loading Road Freight Vehicles
- Paragraph 9.1 is a new paragraph on the importance of verbal communication
- Paragraph 9.2 was updated with the new Seveso directive.
- Paragraph 9.3 adds a recommendation to do a risk analysis on discharge and storage facilities, plus a description of the main requirements for discharge facilities.
- Paragraph 9.5 adds the requirement to have a hose maintenance programme
- Paragraph 9.7 the table called "recommended procedures for unloading of tank containers" has been fully updated to reflect the responsibilities for both the driver and the Receiver/Receiver's operator

#### Chapter 10:

- Paragraph 10.1 Size of new tanks is recommended to have sufficient capacity to unload the ordered volume
- Paragraph 10.9 New paragraph on safe working at heights

#### Chapter 11:

- Paragraph 11.2 is new and explains the use of the Mutual Aid Scheme
- Paragraphs 11.4-11.5 were taken out. Information can be found in The Convention for Providing Mutual Aid in the Case of Incidents during the Transport (and Unloading) of TDI and MDI

Appendix 2 is new and talks about why top discharge for isocyanates is preferred

Appendix 3 is new and is an example of an unloading checklist

# Contents

# Foreword

### **1. Introduction**

1.1	Purpose	07
1.2	Products	07
1.3	Scope	07
1.4	Transport Safety	07
1.5	Adoption	08

# 2. Main Properties, Hazards and Safety Information

2.1	Appearance	09
2.1.1	TDI	09
2.1.2	Polymeric MDI	09
2.1.3	Monomeric MDI	09
2.2	REACH	10
2.3	Main Physical / Chemical Hazards	10
2.4	Health Hazards and First Aid	11

# **3. Personal Protective Equipment**

3.1	Recommended Personal Protective Equipment to Transfer TDI/MDI Products	12
3.2	Emergency Equipment	13

# 4. Design and Construction of Bulk Transport Equipment

4.1	Bulk Transport Equipment	14
4.1.1	Top Fill and Top Discharge	14
4.1.2	Tank containers, Isotanks and Swap Bodies	14
4.1.2.1	Fall Protection	14
4.1.3	Tank containers and Isotank Equipment	16
4.1.3.1	Couplings, Openings and Ancillary Equipment	16
4.1.3.2	Pressure Relief and Vacuum Valves	16
4.1.3.2.1	Pressure Relief Valves – Tank containers	16
4.1.3.2.2	Pressure Relief Valves – Tank Containers	17
4.1.3.2.3	Vacuum Relief Valves	17
4.1.3.3	Transport Equipment Humidity Conditions	17
4.1.3.4	Thawing and Heating Systems	17
4.1.3.5	Sample Tubes – Sampling	18

# 5. Safety Auditing of Road Carriers and Tank Operators

5.1	Carrier Capability: Assessment and Control	19
5.2	Safety and Quality Assessment System	19
5.3	Meeting Safety and Regulatory Standards	19

# 6. Training for Drivers

6.1	Specific Requirements for TDI / MDI	20
6.2	General Product Information	20
6.3	Loading / Transport / Unloading Recommendations	20
6.4	Technical Proficiency	21
6.5	Spills	21
6.5.1	Minor Spills	22
6.5.2	Major Spills	22
6.6	Liquid Decontaminant Solutions	23
6.7	Fire	23
6.8	Emergency Response	24

# 7. Loading Operations

7.1	Compliance with Modal Transport Regulations	25
7.2	Availability of Written Operating Instructions	25
7.2.1	Verbal communication	25
7.3	80/20 Rule	25
7.4	Loading TDI / MDI with Polyol in Adjacent Compartments	26
7.5	Inspection of Bulk Transport Equipment	26
7.5.1	Routine Inspection of Tank Containers and Tank Containers at Loading Terminals	26
7.5.2	Maintenance of Transport Equipment	28

# 8. Road and Intermodal Transport

8.1	Carrier Responsibilities	29
8.2	Instructions in Writing – only for TDI	29
8.3	Routing	29
8.4	Safe Parking	29
8.5	Severe Weather Conditions	29
8.6	Delays or Accidents	29
8.7	Temperature Checks during the Journey	30
8.8	Multi-Modal Movements	30
8.9	Opening Tank Containers	30
8.10	Reintroduction of Equipment to Service	30

# **Contents (cont)**

# 9. Unloading Operations

9.1	Verbal communication	31
9.2	Responsibilities According to the Provisions of the "Seveso Directive"	31
9.3	Criteria for Discharge Facilities	32
9.3.1	Emergency Stop	32
9.3.2	Weather protection cover	32
9.3.3	Quality of surface	32
9.3.4	Rain water drainage system	32
9.3.5	Collection of spilled product	32
9.3.6	Discharge device	32
9.3.7	Fall protection	33
9.4	Safety Assessment for Unloading and Storage Facilities	33
9.5	Criteria for Discharge Hoses	33
9.6	Operator Protective Equipment	34
9.7	Recommended Procedures for Unloading of Bulk Equipment	34
9.8	Non-Standard Operations (NSO)	44
9.9.1	Direct Discharge from Bulk Equipment into IBCs or Drums	44
9.9.2	Unloading into more than one Storage Tank or incomplete Unloading	45
9.9.3	Insufficient Capacity of Storage Tank	45

# **10. Storage Operations**

10.1	Tank size	46
10.2	Bunding	46
10.3	Inlet Gas	46
10.4	Venting	46
10.5	Level Indicator and Alarm	46
10.6	Pressure/Vacuum Protection	46
10.7	Temperature Control	46
10.8	Circulation	47
10.9	Safe working at height	47

# 11. ISOPA's Convention for providing Mutual Aid in case of incidents during the Transport of TDI / MDI

11.1	Purpose and Scope	48
11.2	Use of the Mutual Aid Scheme	48
11.3	Technical Communication	48
Appendix	1: Reaction of Diisocyanates with Water	49
Appendix	2: Top Fill & Top Discharge	50
Appendix 3: Exemplary checklist for loading/unloading operation		

# Introduction

### 1.1 Purpose

These Guidelines have been prepared by ISOPA (the European Diisocyanate & Polyol Producers Association), a partner association 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 TDI is classified as hazardous for both use and transport and MDI is classified and regulated as hazardous only for use, 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 include 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 tank containers, isotanks and swap-body tank 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 tank containers, inland waterway barges or 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 that transport TDI and/or MDI should train their drivers who transport TDI and/or MDI using the ISOPA driver training package (<u>http://www.isopa.org/product-stewardship/logistics/driver-training-for-carriers/</u>). Training should be organised such that drivers are trained in their mother language or in a language they are able to understand and speak. Once a driver has been certified it is the carrier's responsibility to ensure that the driver remains at a satisfying level of knowledge by operating on a regular basis.

Customer collection of TDI / MDI is not advised. If unavoidable, then only carriers participating in the ISOPA driver training programme 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.



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



#### 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 REACH

If you use the substances or formulated chemicals inside the EU, Norway, Iceland or Liechtenstein, you need to comply with REACH\*

If you imported the substances or formulated polyols, the importing legal entity needs to comply with registration requirements.

If you reimport or receive chemicals from inside EU, Norway, Iceland or Liechtenstein, the REACH – Regulation requires you to check the compliance of your supplier.

All relevant information, such as the REACH registration number and the uses covered, is available from your suppliers' safety data sheet.

If you use registered substances inside EU, Norway, Iceland or Liechtenstein, you are considered to be a downstream user within the REACH-Regulation (EC).

The REACH-Regulation(EC) is not mandatory if you use chemicals outside theEU, Norway, Iceland or Liechtenstein.

For relevant scenarios please consult the safety data sheets of your supplier.

For more information please consult: http://www.isopa.org/eu-policy/reach/

\*REACH is the European Community Regulation on chemicals and their safe use (EC1907/2006). It deals with the Registration, Evaluation, Authorisation of Chemicals

### 2.3 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 tank 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 creation 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 tank container exposed to the heat of a fire will decompose with a build-up of pressure, resulting in a risk of the tank container bursting.

# 2.4 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 sought. 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 sensitisation. 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

All necessary protective clothing should be worn and emergency equipment should be available for operations. People should be trained in the correct use of this clothing and equipment. Whenever the driver leaves his tank container, he should wear the minimum required personal protective equipment as a precaution in case of an emergency.

After (un-)loading, the PPE should be taken off completely and stored outside the driver cabin as small undetected spots and drops of isocyanate on the PPE can lead to occupational exposure levels being exceeded.

# **3.1 Recommended Personal Protective Equipment to transfer TDI / MDI products**

	Survey	Connection/Disconnection	Dealing with spillages
MDI	Overall Safety shoes / boots Gloves fit for chemical products Goggles	Hard hat Goggles Chemical protection gloves (EN 374 Cat. III) fit for chemical products Safety shoes / boots Overall	Hard hat Self breathing apparatus Chemical protection gloves (EN 374 Cat. III) fit for chemical products Safety shoes / boots Full chemical suit
TDI	Overall Safety shoes / boots Gloves fit for chemical products Goggles	Hard hat Full face mask with appropriate filter: AP2 as minimum Chemical protection gloves (EN 374 Cat. III) fit for chemical products Safety shoes / boots Full chemical suit	Hard hat Self breathing apparatus Chemical protection gloves (EN 374 Cat. III) fit for chemical products Safety shoes / boots Full chemical suit

MDI



TDI







### 3.2 Emergency equipment

The industry standard for loading / unloading sites is to have an emergency shower and eyewash available close (< 10m) to the discharge location with easy, unhampered access. Also recommended is an emergency stop button on each loading station (relevant recommendation for the installation, not part of PPE). In case of an emergency, e.g. a TDI or MDI loss of containment, drivers and operators at the emergency location should evacuate the area and trained site personnel should, in full PPE (as described under sections 3.1 and 3.2) and using self-contained breathing apparatus rather than a filter mask, deal with the incident.

Drivers should always have an eyewash bottle in the tank container for emergencies during the transport of Diisocyanates.

# 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 the loading and unloading point is reduced
- The risk of damaging the fittings during handling (tank 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 Tank Containers, Isotanks and Swap Bodies

Tank container, isotanks and swap-bodies used for the carriage of TDI / MDI must fulfil the design and construction requirements of national and international regulations (e.g. ADR & IMDG). Producers and carriers should agree on a standardised specification of the fleet.

In addition, the frame of isotanks and swap-bodies must have a valid CSC (Convention of Safe Containers) plate or they must be checked inside the Accepted Continuous Examination Program (ACEP).

The use of multi-compartment tank containers 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 one is 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 achieved 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 to be adequate fall protection and is considered to be 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 to be 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 anchor 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 to be hazardous.

When looking to reduce fall-related incidents and consequences thereof, the first measure to consider is avoiding work on top of transport equipment. This is a potential issue when it comes to Disocyanates where top loading and unloading is required for security and quality reasons. Ground operated tanks are used for Polyol transport only.

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 of preventing falls. 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. they are adjusted / adjustable to the height of the transport equipment
- 2. they do not interfere with overhead structures
- 3. they 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.
- 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 tank container is used, the harness needs to be attached to a retractable lanyard before climbing the ladder.
- 4. A potential rescue operation needs to be assessed at the site where the operation takes place. This requires that the operation is not carried out unattended. Rescue must be carried out within five minutes of the fall to prevent suspension trauma.
- 5. Correct usage of the harness is essential. Training should be provided by the organisation 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 organised by the carrier. If the driver is handed a harness at the site, the site organisation will provide and document the training. That organisation is also required to inspect the harness and lanyard in accordance with the manufacturer's instructions.

# **4** Design and Construction of Bulk Transport equipment

#### 4.1.3 Tank Containers and Isotank Equipment

In addition to the standards required by regulations cited under 4.1.2, tank containers 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 tank containers are clearly labelled. Minimum requirement is to have the couplings for Liquid, Pressure and Vapour in one spill tray with cover.

The dip pipe connection should be marked with "LIQUID" and the vapour return connection with "VAPOUR". Markings should be on a engraved plate on the spill box 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. A fourth flange should be marked as spare.

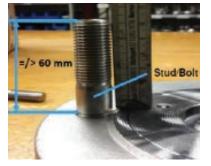
All couplings must be secured by a blind flange/slotted flange or protective cap and appropriate gasket (PTFE or EPDM gaskets recommended) or another system providing equal protection

The following fittings must be available:

**Manlid:** 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 (size M16 and length =/> 60mm). The screw threads of the stud bolts have to be in good condition.







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.

#### 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 – Tank Containers

Fitting of pressure relief valves on tank containers 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 tank container is fitted with pressure relief valve(s), the valves must be preceded by bursting disc(s) with a higher design pressure than the relief valve and manometer(s) to indicate disc rupture.



EPDM



#### 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 can be applied to discharge the TDI or MDI (dew point < - 20° C corresponding to approximately 1,020 ppm of water). The pressurised dry air or nitrogen should be provided by the consignee and should not exceed two (2) bar. The pressure should be ensured by means of safety valves.

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, please consider the heat loss (1°C to 6°C per day depending on ambient temperature and insulation). Check the temperature during transport and before reaching the unloading area against the supplier specifications (minimum temperature / maximum temperature and max. contact temperature, if necessary heat the material as described below.

# **Remark:** Several product grades require different temperature settings. For detailed information, you should consult your supplier.

Freezing TDI will separate the isomers. Contact your supplier.

The best way to thaw frozen TDI and MDI is with water at 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 content 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 as well as the carrier both fully understand 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.

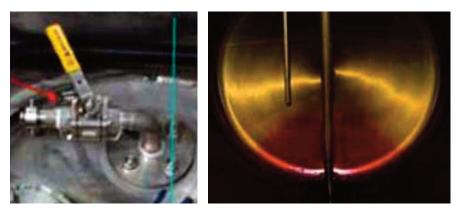
The supply cable for electrical systems on isotanks and tank containers should terminate in a 5-pin plug (32 amp. 6h) or 4-pin plug (63 amp. 6h).

# **4** Design and Construction of Bulk Transport equipment

#### 4.1.3.5 Sample Tubes – Sampling

Sample tubes in tank containers and tank containers 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. Please be aware that taking a sample using this method does not guarantee a representative sample of the full shipment. Therefore it's recommended not to take samples anyway.

Samples accompanying the tank container are not recommended either. They are not representative of the content of the tank container and may pose safety risks during transport.



# **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 vitally important that the chemical company is assured that the carriers being employed are competent and operating to appropriate safety standards. Although ISOPA advises that customer collection of TDI / MDI should not take place, if it is unavoidable, 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 regarding the operational acceptability of the carriers. This can be done by auditing. Next to using tools like CEFIC's Safety and Quality Assessment System (SQAS) for Road Haulage, specific TDI / MDI aspects like driver training, HSSE performance and incident records should be taken into account.

# 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 / 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 and passed the questionnaire as specified in the ISOPA Driver Training program (<u>http://www.isopa.org/product-stewardship/logistics/driver-training-for-carriers/</u>) and that those trained drivers are driving TDI / MDI loads on a regular basis to ensure that the gained knowledge is alive. Training should be provided in either the mother language of the driver or a language they understand and speak.

# **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:

• 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

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 loading and unloading, the producers insist that there should be a well-defined division of responsibilities between the driver and site operators. Given a range of severe incidents that were caused by, among others, poor communication between both parties and a lack of understanding of procedures, drivers should not have the leading role in loading and/or unloading activities.

The main responsibility for a safe loading/unloading process falls to the supplier loading/customer unloading operator.

The main responsibility for safe transport falls to the transport company and the supplier.

Although the unloading process should be seen as a shared responsibility between the consignee and the driver, the main responsibility for a safe unloading process falls to the consignee of the goods.

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

Before starting loading, transport or unloading: take the time to become well acquainted with the fittings and equipment associated with the tank container and the local conditions, specifically:

#### Loading and Unloading operator:

 The handling of all fittings, couplings and the equipment associated with the tank container, 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.

#### **Driver:**

- The heating system of the tank container in order to maintain the product within the temperature limits specified by the supplier or customer.
- The company regulations and safety installations (escape routes, emergency stop buttons, safety shower, eye wash bottles, fall protection etc.) on the loading and unloading stations under instruction of the company personal.

#### 6.5 Spillages

In considering the various aspects of spillage, it is necessary to distinguish between minor spillages and major spillages. The most important factor for distinguishing between them is the ability of people to deal with the occurrence on the spot.

Values for the spillage variation:

#### Minor spill:

- Less than 1 Kg Dangerous Goods
- Less than 25 Kg Non-Dangerous Goods

**Definition:** An event that can be handled safely without the assistance of the Environmental Health and Safety Office or emergency response personnel.

#### Major spill:

- More than 1 Kg Dangerous Goods
- More than 25 Kg Non-Dangerous Goods

**Definition:** An event that cannot be handled safely without the assistance of the emergency response personnel, including all events where a person is injured or contaminated.

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** Training for drivers

#### 6.5.1 Minor Spillages

- Secure the Area
- Clear the area of all non-essential people
- Inform the supervisor, Environmental Health personnel and Safety Office of the operation
- Put on respiratory protection in addition to the Personal Protective Equipment described in Sections 3.1 and 3.2
- Prevent further spill if possible, but without taking any personal risks
- Cover the spillage with absorbent materials such as absorption granules, wet sand, wet earth or clay and shovel the mix in open waste containers, if spilled material is left over repeat the exercise.
- Pour liquid decontaminant (see Section 6.6) over the spillage and allow the mix to react for at least 30 minutes
- Clean the area from the last contamination
- 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
- Inform supplier about the issue and lessons learned

#### 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 vapor and contamination of equipment
- Provide First Aid if applicable
- Prevent access
- Notify emergency services immediately\*
- The use of self-contained breathing apparatus by the emergency team members is a requirement. Ensure sufficient breathing equipment is available for a team of responders.
  - \* In case 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 created by 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 liter). However, other open top containers could be used as well. Drums should only be filled to 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.
- Inform supplier about the issue and lessons learned

# 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 spills 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. The larger the amount of TDI / MDI to be neutralised, the more critical this becomes. This precaution is necessary because the reaction may generate heat resulting in an increased creation 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 neutraliser 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, including the driver
- Keep up-wind to avoid inhalation of vapour and contamination of equipment
- 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 everyone fighting the fire. It is crucial that self-contained breathing apparatus is 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 first responders in transport incidents and in 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/product-stewardship/logistics/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.

# 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 tank containers, isotanks and swap-body containers. Those 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 an emergency. Drivers should be familiar with safety procedures, including site alarms and the use of safety equipment at the loading point.

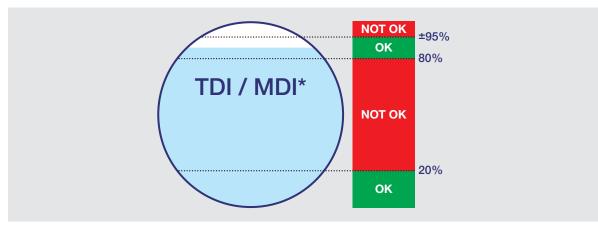
#### 7.2.1 Verbal communication

The increasing diversity of languages spoken by drivers in the industry is adding to this communication issue, the impact of which is particularly felt in an emergency situation. This is why it is critical that drivers must have sufficient language skills to be able to communicate with the loading/unloading site staff, preferably in the local language(s) of the site or in (basic) English/French/German. If the driver is not able to communicate with the site staff in a sufficient way, the loading/unloading cannot take place.

# 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 tank containers and impairs the tank container stability. It is not related to the hazardousness of the product. Thus, it is strongly recommended to also apply this rule to any tank containers 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** Loading Operations

# 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 if 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 to 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.

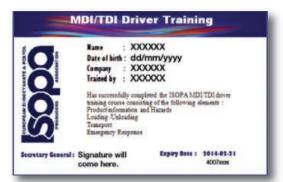
In addition to the routine inspection of all bulk transport equipment prior to each loading operation, a responsible person from the loading company should carry out a check on each tank container or isotank prior to its initial introduction, or reintroduction into service after maintenance or repair.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

# 7.5.1 Routine Inspection of Tank Containers 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?
- Check that the tank container capacity is adequate for the quantity to be loaded and that, when loaded, ullage and maximum allowed gross tank container 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<sup>®</sup>, the design of bulk transport units carrying MDI should remain the same as before the declassification of MDI.

#### **Expeditionary checks**

#### Site entry checks

- 1. Identification of driver / tank container crew
- 2. Identification of tank container
- 3. Identification of tank container compartment number
- 4. Transport order (order-no., load reference)
- 5. Check weight
- 6. Valid TÜV / technical tank container inspection
- 7. Driver adequate
- 8. No forbidden items / materials
- 9. No forbidden people / passengers
- **10.** Personal protective equipment for each member of the tank container crew complete and appropriate
- 11. DG related: valid ADR license available
- 12. DG related: Instruction in writing available
- 13. Design approval /TC certificate / BGTC available and OK
- 14. Adherence of driving time / rest period

#### **Technical Checks**

- 1. CSC Plate / ACEP available
- 2. Valid TÜV / technical tank container inspection
- 3. Check heating devices and temperature control
- 4. Tyres OK
- 5. Tank container lightning OK
- 6. Underride barrier OK
- 7. Windscreen in the driver's field of sight free of damage
- 8. No contamination outside the tank
- 9. No other obvious safety relevant deficiencies tank container body
- 10. Tank container free of logos, labels etc. associated with / advertising for food

#### **Dangerous Goods checks**

- 1. Orange-coloured plates available
- ADR personal protective equipment for the tank container crew complete and without any deficiencies
- 3. ADR tank container equipment complete and without any deficiencies
- 4. ADR fire fighting equipment complete and without any deficiencies

# **7** Loading Operations

#### Expeditionary checks (cont)

#### **Preload Checks**

- 1. Prevous product confirmation / cleaning certificate
- 2. Filling grade
- 3. Dome cover / Manhole area / spill tray OK
- 4. Ascension pipe / filling pipe OK
- 5. Fittings and flanges OK freedom of movement
- 6. Length of bolts OK
- 7. Labelling of flanges
- 8. Technical Devices OK
- 9. Heating / Temperature Control OK
- 10. Chambers and devices marking / labeling complete and correct
- 11. Grounding working
- 12. Self-loading permit available if relevant
- 13. Bulk-Loading Isocyanates: ISOPA License available

#### Load End Checks

- 1. Closure and leak tightness tank (incl. gaskets / devices confirmed)
- 2. Permissible degree of filling resp. load balance (multi-compartments) OK
- 3. No outside contamination
- 4. Load Securement OK
- 5. Tank container / Transport Unit closed properly and sealed
- Warning signs / Orange-coloured plates (neutral or with hazard identification / UN number) opened / closed as required
- 7. Placards / DG Marking and labeling applied and correct
- 8. Maximum allowable payload not exceeded
- 9. Shipping documentation checked and handed over to driver

#### **Reintroduction to service**

See Section 8.10.

#### 7.5.2 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 emergency situation that may occur during carriage, instructions in writing in the form specified in Section 5.4.3.4 of ADR shall be carried in the tank container crew's cab and shall be readily available.

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

Before the start of the journey, the members of the tank container 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 tank containers transporting TDI or MDI must, whilst on the road, ensure that the tank container, 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 tank containers 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 tank container must stop at the next suitable parking place. The tank container 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 tank container, or product spill, or potential loss of containment, the driver and carrier must follow the company's

# 8 Road and Intermodal Transport

emergency response procedure and, in the 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, 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 .

If the temperature of the tank contents rises 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 arrival at the consignee.

### 8.8 Multi-Modal Movements

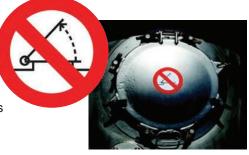
For multi-modal carriage that is not driver / tractor accompanied during the rail-sea stage, particular attention must be given to ensure that the tank container used for the final delivery is properly labelled with the appropriate placards and – only for TDI – carries appropriate instructions in writing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

The consignor should consider carrying out a safety assessment at the container terminal 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 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:

Check that maintenance and repairs have been carried out effectively and compare them with the work requested.

Has the tank been properly cleaned? (availability of certificate of cleanliness e.g. European cleaning certificate ECD).

Check that measures have been taken to ensure that the compartment atmosphere has a dew point of < -20  $^{\circ}$ C.

Are all openings closed and are all bolts present and correctly tightened?

# **9** Unloading Operations

Responsibilities according to BBS-Guidelines (Behaviour Based Safety):

The roles and responsibilities in loading and unloading operations are described in the CEFIC-ECTA-FECC "Best Practice Guidelines for Safe (Un)loading of Road Freight Vehicles covering Technical, Behavioural and Organisational Aspects" (2013):

#### 2.2 "The (un)loading site is responsible for all activities and is required to take appropriate measures so that all persons – including any from outside undertakings – engaged in on-site operations work can do so safely. This includes the entire (un)loading operation."

The present guidelines follow the principles and logic of these CEFIC-ECTA-FECC guidelines and seek to apply them specifically to unloading operations for TDI and MDI in bulk.

# 9.1 Verbal communication

The increasing spread in languages spoken by drivers in the industry is strengthening this communication issue, the impact of which is particularly felt in an emergency situation. This is why it is critical that drivers must have sufficient language skills to be able to communicate with the loading/unloading site staff, preferably in the local language(s) of the site or in (basic) English/French/German. If the driver is not able to communicate with the site staff in a way deemed sufficient, the loading/unloading cannot take place.

#### 9.2 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, then updated in 1996 (96/82/EC) and in 2012 (2012/18/EU) is generally known as the "Seveso Directive", provides the members of the European Union 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 important to all members of the polyurethane industry who process and store TDI in quantities above defined limits which are currently 10 tonnes and restricted to a maximum of 100 tonnes. 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 people working on the site with safety information, training and the appropriate equipment:
  - to prevent major accidents (i.e. spills 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

In line with the Seveso requirements, a review by ISOPA of a number of incidents that happened during loading and unloading activities took place in 2014. These showed that critical communication between operator and driver is severely hampered by the mandatory use of a full face filter mask.

# **9** Unloading Operations

# 9.3 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)

Furthermore, it is recommended that a risk analysis (HAZOP) is performed of the discharge and storage facilities, to identify hazards and malfunctions, in order to enable suitable modifications to accomplish safe and reliable procedures. To avoid risks associated with changes, it is essential to have an integrated and systematic Management of Change (MOC) process.

It is not the intention of these guidelines to provide detailed engineering advice on the design of TDI / MDI discharge facilities. Discharge 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 discharge facilities are described below.

#### 9.3.1 Emergency Stop

The discharge operation must be stopped immediately, in a safe and effective manner in case of emergencies. Therefore, it is imperative to have an automatic emergency-stop-system.

#### 9.3.2 Weather protection cover

The discharge area should be covered, to protect operators and equipment against strong weather conditions and associated risks.

#### 9.3.3 Quality of surface

The surface of the discharge area should be built in a resistant and liquid-tight way. Commonly used materials are liquid-proof concrete or asphalt.

#### 9.3.4 Rain water drainage system

The rain water drainage system of the discharge area should be closed or covered during discharging operation, in order to prevent impurities/ contamination of ground water in case of spills.

#### 9.3.5. Collection of spilled product

A spillage-containment area should be available to hold back major spillages and to protect the environment and ground water. The capacity of the containment should be sufficient for one full truck. The discharge operation should be continuously supervised and should be effectively stopped in the case of an emergency.

#### 9.3.6 Discharge device

It's recommended to use unloading-arms to ensure a safe and professional discharge operation. When using hoses for discharge – a lifting device, preferably operated by one person, should be available. It is recommended to always use new gaskets for each discharge operation.

#### 9.3.7 Fall Protection

For all works on top of transport equipment, it is mandatory to have an appropriate fall protection (e.g. unloading platform with guard rails and stairs, fall restraint system with anchor point). A collapsible handrail is not considered as adequate fall protection. Please see further remarks in chapter 4.1.2.1 "Fall Protection".

# 9.4 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, in cooperation with the customer, arrange a safety assessment of the customer's unloading and storage facilities prior to an initial delivery and at three year 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 <u>www.isopa.org</u>. 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.

# 9.5 Criteria for Discharge Hoses

It is strongly recommended that customers own all discharge hoses and vapour return hoses required for product discharge, that these are specifically selected for TDI / MDI service and are fitted with a ball valve at the tank container-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 (ideally DN50) proportionate to the pump capacity and should be connected to the DN50 vapour return connection.

The customer is required to have a maintenance plan in place for the maintenance of all the hoses. The hoses should be tagged with the most recent inspection date.

	Hose type	Saturn SP EPDM EN 12115	
10 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Material inside	EPDM, black, smooth	
0000	Material inside	EPDM / CR	
-	Nominal diameter	50mm	
<b>6</b>	Total length	6000mm	
	Max work pressure	16 bar	
	Test pressure	21 bar	
	Test vacume	-0.9 bar	
	Bursting pressure	48 bar	
	Temperature range	-35°C / + 100°C	

# 9.6 Operator Protective equipment

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

# 9.7 Recommended Procedures for Unloading of Bulk equipment

Bulk discharge should preferably be carried out by means of pumps rather than pressurised dry air or nitrogen. Tank containers 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.

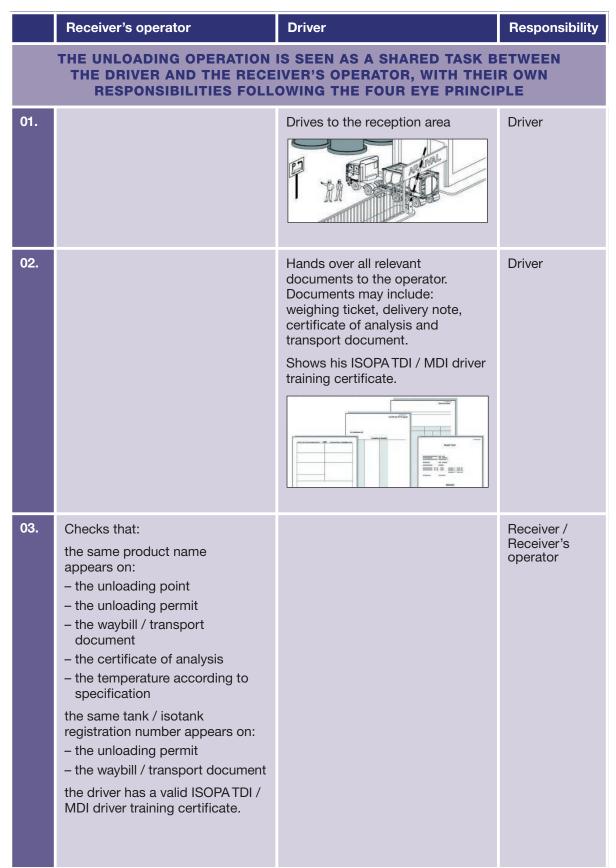
If a pump is used for product discharge, it is preferable to use a seal-less type (e.g. magnetic driven pump). However, mechanical seal pumps are also acceptable. If a positive displacement pump is used it should be fitted with a pressure relief valve with the discharge on the suction side of the pump.

The discharge facility must be constructed adequately in order to prevent vacuum conditions in the tank container 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. It is recommended that the receiver's operator uses a written checklist for the discharge operation.

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 tank container. 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 Tank Containers**



#### **Recommended Procedures for Unloading of Tank Containers**

	Receiver's operator	Driver	Responsibility
04.	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		Receiver / Receiver's operator
05.	Checks the weight to be unloaded on the unloading permit. Makes sure that the reception tank can accommodate the load.		Receiver / Receiver's operator
06.		Positions his tank container, as far as possible, ready for emergency evacuation.	Driver
07.		Ensures wheels are blocked with two (2) chocks.	Driver
08.		<ul> <li>Prepares tank container for unloading:</li> <li>shuts off the engine</li> <li>applies the handbrake</li> <li>place truck at horizontal position or at slight gradient</li> </ul>	Driver
09.	Installs signs in front and behind the tank container indicating that a product transfer is taking place.		Receiver / Receiver's operator

	Receiver's operator	Driver	Responsibility
10.	The receiver and the driver put on the driver pu	neir individual protective equipment.	Receiver / Receiver's operator Driver
11.	<ul> <li>Tells the driver where to find:</li> <li>the safety shower and eyewash</li> <li>the fire extinguisher</li> <li>the emergency stop button</li> <li>the telephone or intercom and briefs the driver on site emergency procedures</li> </ul>		Receiver / Receiver's operator
12.	In case of disagreement, the receive – refuses to unload – informs the site road traffic office – each consults his superior for inst – notes the incident in the events re	and the carrier's planner ructions	Receiver / Receiver's operator Driver
13.	Installs the gangway providing safe access to the top of the tank container. Alternatively, prepares the fall arrest system for use.		Receiver / Receiver's operator
14.		The driver opens the cover of the spillage tray of the tank container.	Driver

	Receiver's operator	Driver	Responsibility
15.	<ul> <li>Ensures that all tank container valves are fully closed, together with the driver</li> </ul>	<ul><li>b. Visual check with the receiver's operator to ensure that all tank container valves are fully closed.</li><li>c. Removes blind flanges or caps from all outlets.</li></ul>	Receiver / Receiver's operator
16.	Checks that site equipment – e.g. product hose, vapour return or nitrogen/air pressure line, couplings, gaskets and seals – are in good condition, fit for purpose and carry out a visual check on the internal cleanliness.		Receiver / Receiver's operator
17a.	FOR PUMP DISCHARGE ONLY: W	ith a vapour return line	
	<ul> <li>c. Ensures the pump versus vapour flow capacity is such that the pressure in the transport tank is never below atmospheric conditions</li> </ul>	<ul> <li>a. Installs the vapour return line connection to the tank container.<sup>(1)</sup></li> <li>b. Ensures valves on the vapour return line are open.<sup>(2)</sup></li> </ul>	Receiver / Receiver's operator
	<ul> <li>e. Operator and driver to ensure valves on the liquid line are open.<sup>(4)</sup></li> <li>f. Operator and driver to agree that the installation is safe and ready for the discharge.<sup>(5)</sup></li> <li>g. The operator to start the unloading operation</li> </ul>	<ul> <li>d. Installs the liquid line connection to the tank container.<sup>(3)</sup></li> <li>e. Operator and driver to ensure valves on the liquid line are open.<sup>(4)</sup></li> <li>f. Operator and driver to agree that the installation is safe and ready for the discharge.<sup>(5)</sup></li> </ul>	

	Receiver's operator	Driver	Responsibility
17b.	FOR PUMP DISCHARGE ONLY: If	no vapour return line exists	
	a. Ensures the dry air flow capacity is such that the pressure in the tank container is never below atmospheric conditions.	b. Connects and opens the tank container air vent to the receiver's dry air / nitrogen supply.	Receiver / Receiver's operator
18.	FOR PRESSURE DISCHARGE ON	LY:	
	<ul> <li>a. Ensures the dry gas supply is free of impurities, especially water, rust, etc.</li> <li>b. Ensures the dry air pressure does not exceed two (2) bar.</li> <li>c. Connects the dry air / nitrogen (for monomeric MDI, nitrogen is preferred) to the tank container.</li> </ul>	Assists the receiver's operator.	Receiver / Receiver's operator
19.	Checks the presence and state of the couplings and gaskets and connects the unloading arm or flexible hose by performing a pressure test and relieves the pressure after the test in a safe manner.	Assists the receiver's operator.	Receiver / Receiver's operator
20.	Opens the hose or unloading arm valve.		Receiver / Receiver's operator

	Receiver's operator	Driver	Responsibility
21.	TOP DISCHARGE BY PUMP:		
	<ul> <li>a. If the Storage tank is under pressure, checks the presence and state of the couplings and gaskets and connects the unloading arm or flexible hose by performing a pressure test and relieves the pressure after the test in a safe manner.</li> <li>c. Opens the valve on the</li> </ul>	b. Opens the tank container outlet valve.	Receiver / Receiver's operator
	receiver's line.		
22.	TOP DISCHARGE BY PRESSURE:		
	<ul><li>a. Opens the dry gas supply valve.</li><li>c. Opens the valve on the</li></ul>	b. Opens the tank container dry gas inlet valve.	Receiver / Receiver's operator
	receiver's line when pressure has built up in the tank container.	d. Opens the tank container	
		outlet valve when pressure has built up in the tank container.	
23.	VALID FOR BOTH PROCEDURES:		
	<ul> <li>a. Observes and controls the transfer during the whole unloading process, including the product level in the reception tank. If any anomaly linked to product discharge is detected, the receiver must: <ul> <li>immediately stop the discharge</li> <li>inform management and seek instructions</li> <li>record the incident in the register of events</li> </ul> </li> </ul>		Receiver / Receiver's operator
		<ul> <li>b. Attends the tank container during transfer to observe and assist in any emergency.</li> <li>The driver should not stay on top of the container.</li> </ul>	

	Receiver's operator	Driver	Responsibility		
	AT THE END OF T	HE TRANSFER OPERATION:			
24.	TOP DISCHARGE BY PUMP:				
	<ul><li>a. Manipulates the hose to provide gravity flow to the pump enhancing hose drainage.</li><li>b. Closes the valve on the receiver's line.</li><li>c. Stops the pump.</li></ul>	d. Shuts off the tank container connections and disconnects the hose from the tank container after drainage.	Receiver / Receiver's operator		
25.	TOP DISCHARGE BY PRESSURE:				
	<ul> <li>a. Closes the dry gas supply valve.</li> <li>b. Disconnects the dry gas supply line.</li> <li>c. Allows the tank container to decompress via the receiver's cargo line to maximum of 0.2 bar.</li> <li>d. Closes the valve on the receiver's line.</li> </ul>	e. Shuts off the tank container connections.	Receiver / Receiver's operator		
AL	WAYS CHECK IF THE TRANSPO PRESSURE BEFORE MAKING	ORT TANK AND/OR EQUIPMENT G OR BREAKING ANY CONNECT			
26.	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.	Assists the receiver's operator actions.	Receiver / Receiver's operator		
27.	In case of spills, the operator cleans the spill tray.		Receiver / Receiver's operator		

	Receiver's operator	Driver	Responsibility
28.	Assists the driver's actions.	Refits the gaskets / blind flanges on the tank container connections.	Driver
29.	Withdraws the gangway and locks it in the upper position or stows away the fall arrest system.		Receiver / Receiver's operator
30.	The receiver and the driver remove equipment, carefully checking if any the discharge process.		Receiver / Receiver's operator
31.	<ul> <li>the discharge process.</li> <li>a. Authorises the driver to leave the unloading area.</li> <li>b. The driver should ensure that it is safe to leave the (un)loading area by walking around the tank container and performing a 3-Minute check after discharge.</li> <li>Equipment: <ul> <li>Disconnected?</li> <li>Free of spillages including spillage tray?</li> <li>Safety handrail down?</li> <li>Valves closed and blind- flanged, manlids closed?</li> <li>Spillage tray covers closed?</li> <li>Depressurise at the customer if possible, or inform planner</li> <li>Remove wheel chocks</li> </ul> </li> <li>Documentation: <ul> <li>Transport documentation signed?</li> </ul> </li> </ul>		Receiver / Receiver's operator Driver
	BOTH LEAVE	THE DISCHARGE AREA.	
32.	Measures the product level in the reception tank. Closes all reception circuits.		Receiver / Receiver's operator

#### Example of Discharge instruction document

Arri	val	Driver	Custo
1	Report to the reception at the gate.	1	
2	Hand over all relevant documents to the supervisor.	1	
3	Show the driver the way to the discharge point.		
4	Park the tank tank container at the discharge point / apply handbrake / check horizontal position tank container.	1	
5	Use all required Personal Protective Equipment (goggles, overall, liquid tight gloves, safety boots, helmet).	1	
Disc	Sharge		
6	Access top of the tank container via platform / safety ladder tank container and raise handrail once arrived on top of the tank container.	1	
7	Check that there is sufficient space to unload the tank container in the storage tank (check level indicator!)	1	
8	Connect earthing to tank container (if available).		
9	Ensure that all valves of the tank container are closed.	1	
10	Remove blind flange vapour return valve and connect the vapour return hose. (Clean?)	1	
11	Remove the blind flange (in a controlled way) of the discharge valve. (Check if the outlet is free of product / clean).	1	
12	Remove the blind flange of the discharge hose (in a controlled way) and connect the hose to the tank container. (Check if hose is free of water or dirt, always use a new gasket and always tighten four bolts).	~	
13	Ask permission to start the discharge.	1	
14	Open the vapour return on the tank container and storage tank. (To avoid implosion of the tank container).	1	
15	Open the discharge valve on the tank container and open the discharge valve in the line to the storage tank.	1	
16	Start the customer's discharge pump. (Observe that level in storage tank is rising and continue checking for leaks).		
End	of discharge and departure		
17	When discharge is completed, close all valves of the tank container and the storage tank and stop the pump.	1	
18	Disconnect the vapour return line.	1	
19	Disconnect the discharge hose and refit blind flanges. (First check if hose is empty and drained!!)	1	
20	Clean the flange surface and keep spillage tray clean. Ensure threaded holes in flange are free of product.	1	
21	Refit the blind flange to the discharge line and to the tank container outlet valve. (Open and close valve ones in order to remove product on ball of the valve).	1	
22	Have a final check around the tank container to ensure that it is fit for transport.	1	
23	Ask the supervisor to sign all documents (including any remarks).	1	
24	Ask permission to leave the site.	1	
	CHOIL CON		

# **9** Unloading Operations

#### 9.8 Non-Standard Operations (NSO)

A "standard" delivery to a 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 (NSOs) and be sure to evaluate the operational risks. NSOs 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 NSOs, it is not possible to make an extensive NSO list. However, three regularly occurring NSOs have been identified with suggested control measures as listed below. Carriers are encouraged to report NSOs 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 for support from the supplier.

#### 9.8.1 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 has 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 difference 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
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, the driver should only mention this situation to his planner, who subsequently informs the supplier. If the intention is to directly discharge into IBCs from the tank container without a fixed installation, he should not start and contact his planning department who will get support from the supplier.

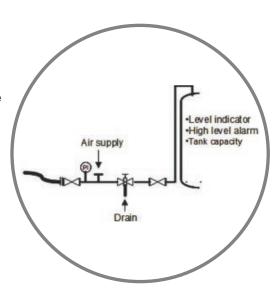
#### 9.8.2 Unloading into more than one Storage Tank or incomplete Unloading

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.

#### 9.8.3 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 and the incident should be recorded by the parties involved. Any partially loaded tank containers 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 unload the ordered volume. 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  $-20^{\circ}$ C.

#### **10.4 Venting**

Any storage tank vents should lead to a safe place outside the storage building and far from the unloading location, 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 to circulate the material by pump. Circulation is also advantageous when the product needs to be heated or cooled.

#### 10.9 Safe working at heights

It is the consignee's responsibility to provide safe working conditions for working at height.

Therefore, it is highly recommended to facilitate one of the following options:

- 1. Safe platform with safety fence
- 2. Safety harness with fall protection
- 3. Mobile stairs with safety fence

For additional guidance please consult the "Best practice guidelines for safe working at height in the logistics supply chain".

# ISOPA's Convention for providing Mutual Aid in case of incidents during the transport of TDI/MDI

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 Europewide 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 convention for providing mutual aid in case of incidents during the transport of TDI / MDI.

#### 11.2 Use of the Mutual Aid Scheme

In the event of any incident occurring during transport of a shipment of MDI and/or TDI which actually causes or potentially could cause damage to persons, property or the environment or prevents the safe continuation of transportation, the affected member company may request any of the other member companies to provide Assistance from an appropriate Emergency Response

- **Level 1** Emergency response Assistance Advice by telephone.
- **Level 2** Emergency response Assistance Advice by experts, if requested, at the scene of the incident.
- **Level 3** Emergency response Assistance Help and provision of equipment at the scene of the incident.

Assistence can include the organisation of equipment which could be needed at the site to deal with the (potential) incident. If the Authorities are in charge of a (potential) incident, the role is to provide technical advice to the Authorities on the nature of the product and on the measures necessary to deal with the (potential) incident, and to provide technical assistance if requested by the Authorities.

#### **11.3 Technical Communication**

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

- Prepare and maintain an Emergency Response Manual.
- Ensure that the training and equipment at participating centres is adequate
- Agree on common methods of approach in the resolution of transport emergency situations
- Safeguard standarisation on equipment.

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.

# **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 carbammic acid (R-NHCOOH) that dissociates as Carbon Dioxide gas (CO<sub>2</sub>) and amines (R-NH2).

The Amine (R-NH2) 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<sub>2</sub> 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<sub>2</sub> 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  $20/18 \times 44 = 49$  kg CO<sub>2</sub> = 27.25 m<sup>3</sup> at 25°C and 1 atmosphere pressure.
- In a 25 m<sup>3</sup> tank container with 20 m<sup>3</sup> 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 isocyanate 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.

# **Appendix 2:**

#### Top fill and Top discharge

For the following reasons ISOPA recommends Top fill and Top discharge of bulk equipment:

- TDI / MDI reacts with moisture from the environmental air with urea and polyurea as a result
- urea and polyurea are solidified products which can easily block valves and other transfer equipment
- when a bottom valve is contaminated with TDI / MDI reacted products it can easily lead to serious leaks
- when a bottom valve of a full loaded TDI / MDI tank container is leaking, it is very difficult to repair and stop the leak
- when there are any problems with a blocked bottom valve during discharge of a TDI / MDI bulk delivery, it is very hard to safely stop the discharge
- the required cleaning frequency for top discharge valves is far lower in comparison to bottom discharge valves. Replacement and maintenance of the bottom valve is only possible after cleaning.

# Appendix 3:

### Exemplary Checklist for unloading operation

Checks before unloading		ок	NOK	Remarks
1	The real tank container Nr. matches with the tank container Nr. listed in the delivery notes			
2	The product name which is listed in the delivery notes matches with the designation/ suitability of intended storage tank			
3	The intended storage tank have sufficient capacity to store delivery volume			
4	Necessary protective clothing is worn			
5	Truck is protected against movement (use of wheel chocks)			
6	Sewer system is closed / containment is activated / unloading area is prepared for unloading / tank container is grounded			
7	The driver has been informed about safety facilities (e.g. emergency shower, eye wash etc.) and sinstructed for emergencies (e.g. push emergency-stop-button etc.)			
8	Operator and the driver wear the instructed protective equipment			
9	Fall arrest system / fall protection is activated			
10	Equipment – e.g. product hose, vapour return or nitrogen / air pressure line, couplings, gaskets and seals – is in good condition, fit for purpose and clean			
11	In case of pressure unloading: Pressure set -2 bar</td <td></td> <td></td> <td></td>			
12	Product hose, vapour return hose (air presure line) are accurately installed and <b>new</b> gaskets are used			
13	All necessary valves (unloading facility + truck) are open and ready for unloading operation			
14	Vapour return valve at truck container is open			
Che	ecks after unloading	ОК	NOK	Remarks
15	Truck container is depressurized			
16	All valves (unloading facility + truck) are closed. All relevant connectors are accurately capped (gasket, blind-flange etc.)			
17	All hoses are disconnected, gas tight closed and stored under dry conditions			
18	Unloading equipment (hoses, gaskets, connectors) is in good condition (visual check) and ready for next unloading			
19	Truck is clean, without any damage, roadworthy and equipped with ADR labels for dangerous goods (in case of TDI)			
20	Truck-wheel-chocks have been removed and loading platform has been lifted			
21	Unloading area is clean / drainage systems activated			
22	Protective cloths are taken off an stored outside the driver cabin			



Contact Rue Belliard 65 B-1040 Brussels Belgium Tel : 32 2 786 35 53 www.isopa.org

The information contained in these Guidelines, and in the documents and recommendations, are believed to be accurate. However, all recommendations are made without any warranty since the conditions of use are beyond the control of ISOPA and its members. ISOPA and its members disclaim any liability in connection with the use of this information. It is the responsibility of the user to verify the accuracy of this information which may be used by the user at his own risk.