



GUIDELINES

For the Safe Transportation, Unloading
& Storage of Packaged TDI & MDI



www.isopa.org

Foreword

The first version of these guidelines, dated October 2013, has been issued by ISOPA's Logistics Working Group under the chairmanship of H. van Wijnen (Huntsman) and A. Vertupier (Vencorex).

The intention is to contribute to overall safety standards by establishing rules for the transport, unloading and storage of packaged aromatic diisocyanates and classified polyols as well as dealing with the empty diisocyanates steel drums.

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

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Consistent with ISOPA's commitment to the principles of Responsible Care, it is recommended that the design of packages and of transport units carrying MDI should remain the same as before the UN's transport declassification of MDI in 1994.

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1. Introduction

1.1. Purpose

These Guidelines have been prepared by **ISOPA** (the European Diisocyanate and Polyols Producers Association) a sector group of **CEFIC** (the European Chemical Industry Federation) to establish appropriately high levels of safety for the transport, unloading and storage of aromatic diisocyanates and certain polyols.

1.2. Products

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

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

The safe handling / transfer of classified polyols are covered in the respective part of this guideline only.

Formulated polyols containing solvents or hydrocarbons are explicitly excluded unless stated otherwise.

1.3. Scope

These Guidelines cover important aspects of unloading and storage activities of packaged TDI and MDI from loading to delivery point. They deal with packed transport units such as tilt trailers, curtain sided trailers, temperature controlled equipment and box containers. Reference to existing regulatory controls like **UN**, **REACH** or **SEVESO** is only made where this is considered necessary for the purpose of clarification.

1.4. Transport safety

The management of the transport company should always supply equipment that is fit for the operation to be carried out and meets all applicable legal requirements.

It should also ensure that drivers are fit for duty and have passed successfully all necessary training to fulfil the legislative requirements and site requirements, in particular regarding the transportation and handling of dangerous goods.

1.5. Adoption

ISOPA recommends that these *Guidelines* are adopted by all parties who are involved in the transport and distribution or receiving shipment of TDI & MDI.



2. Main Properties, Hazards and Safety Information

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

In practice, TDI is sold as 100% 2,4-isomer or as 80/20 , 65/35 or 95/05 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

2.2.1. TDI

	<i>Liquid</i>	<i>Reacted with moisture / water</i>
TDI	Clear to pale yellow, sharp, pungent 	White, foamy 

2.2.2. Polymeric MDI

	<i>Liquid</i>	<i>Reacted with moisture / water</i>
MDI	Brown, slightly musty 	Brown, crusty 

2.2.3. Monomeric MDI

<i>Liquid</i>		<i>Reacted with moisture / water</i>	
MDI	Clear, slightly musty		White, crusty
			

2.2. Regulation on Classification, Labelling and Packaging (CLP)

- Regulation (EC) No 1272/2008 (*CLP Regulation*) is the new EU legislation on classification, labelling and packaging of substances (*mandatory 1 Dec 2010*) and mixtures (*mandatory 1 June 2015*).
- The UN GHS (*Globally Harmonised System for Classification and Labelling of Chemicals*) has been adopted through the **CLP Regulation** replacing the provisions of the Dangerous Substances / Preparations Directives (DSD/DPD) which will be finally repealed by 1 June 2015.
- Product hazards remain the same, but hazard communication changes.

2.2.4. MDI label information



Signal word: Danger

Hazard statements

H332	Harmful if inhaled.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H334	May cause allergy or asthma symptoms or breathing difficulties.
H317	May cause an allergic skin reaction if inhaled.
H335	May cause respiratory irritation.
H351	Suspected of causing cancer.
H373	May cause damage to organs through prolonged or repeated exposure.



Precautionary Statements

P260	Do not breathe dust / fume / gas / mist / vapours / spray
P280	Wear protective gloves / protective clothing / eye protection / face protection.
P285	In case of inadequate ventilation wear respiratory protection.
P302 + P352	IF ON SKIN: Wash with plenty of soap and water.
P304 + P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P309 + P311	IF exposed or if you feel unwell: Call a POISON CENTER or doctor/physician.

Any supplier may prioritize and limit the number of P-statements on the label to 6.

2.2.5. TDI label information



Signal word: Danger

Hazard statements

H315	Causes skin irritation
H317	May cause an allergic skin reaction
H319	Causes serious eye irritation
H330	Fatal if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H335	May cause respiratory irritation
H351	Suspected of causing cancer
H412	Harmful to aquatic life with long lasting effects



Precautionary Statements

P273	Avoid release to the environment
P280	Wear protective gloves / protective clothing / eye protection / face protection
P284	Wear respiratory protection
P285	In case of inadequate ventilation wear respiratory protection
P501	Dispose of contents/container to (hazardous or, special waste collection point
P308+P313	If exposed or concerned: Get medical advice / attention.
P403+P233	Store in well-ventilated place. Keep container tightly closed

Any supplier may prioritize and limit the number of P-statements on the label to 6.

2.3. REACH

- If you use the substances or formulated chemicals inside EU-Europe, Norway, Iceland or Liechtenstein you need to comply with REACH*.
- If you imported the substances or formulated polyols the importing legal entity need to comply with registration requirements.
- If you reimport or receive chemicals from inside the inside EU-Europe, 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 on the uses covered, is available from your suppliers safety data sheet.

- If you use registered substances inside EU-Europe, Norway, Iceland or Liechtenstein you are considered downstream user REACH-Regulation (EC).
- REACH-Regulation (EC) is not mandatory if you use chemicals outside EU-Europe, 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/isopa/index.php?page=reach>

*) REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the **Registration, Evaluation, Authorisation and Restriction of Chemical substances**.

2.4. Main Physical / Chemical Hazards

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

Water

TDI / MDI react with water to produce carbon dioxide and a biologically and chemically inert solid, known as a polyurea. While this is not in itself a dangerous reaction, it can lead to the development of excessive pressure inside closed containers. Eventually, this may even burst the drum / IBC 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 diisocyanates with water including associated pressure increase are described in Appendix 1. The reaction with water is accelerated by other chemicals as described below.

Other chemicals

The contamination of TDI / MDI with other chemicals must be avoided at all times!

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

Rubber and plastics

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

In a fire

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

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

2.5. 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 irritate the eyes, causing watering and discomfort. Splashes of liquid TDI / MDI in the eyes could cause severe irritation if not immediately washed out with large amounts of water for at least 15 minutes. Medical attention should be obtained. Protective equipment must be worn as described under section 3.1 Drivers and operators should not wear contact lenses when handling diisocyanates, but should wear glasses instead.

Skin contact

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

Swallowing

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

Long-term health effects

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

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

More safety information:

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

3. Personal Protective Equipment

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

3.1. Protective Equipment for handling TDI and MDI products

	<i>Handling closed packagings</i>	<i>Handling/Cleaning open packagings</i>	<i>Dealing with spillages</i>
MDI	Hard hat Overall Safety shoes / boots Gloves Goggles	Hard hat Goggles Liquid-tight gloves Safety shoes / boots Overall	Hard hat Self breathing apparatus Liquid-tight gloves Safety shoes / boots Full chemical suit
TDI		Hard hat Full face mask with appropriate filter : AP2 as minimum Liquid-tight gloves Safety shoes / boots Full chemical suit	

Participate in TDI or MDI specific training programs such as Walk the Talk.



For further detailed information see the website of ISOPA (www.isopa.org)

3.2. Emergency Equipment

In case of an accidental release (i.e. spillage) the protective equipment described under Section 3.1 should be worn by all persons dealing with the incident

3.3. Handling in extreme high temperature (> 40°C)

Although at extreme outside temperature it can be very uncomfortable to wear the required PPE it is mandatory to be equipped with the PPE as described in par 3.1.

When necessary the work must be suspended to avoid fatigue to the operator and risk of dizziness/fainting. When dealing with a spillage, periodic replacement of the operator shall be take into account their welfare

4. Handling TDI or MDI in steel drums and MDI in intermediate bulk containers (IBCs)

4.1. Drums

Diisocyanates are shipped in **215 litres** drums with a non-removable head (UN/1A1/ *). These drums have a ¾-inch bung for venting and a 2-inch bung for filling/discharge. Drums with a removable head should never be used for diisocyanates.



*) The industry agreed to use UN certified packagings only. For TDI this is a legal requirement.

Drum shipments of diisocyanates may require heated trucks in certain geographic locations. Drums should be stored in a well ventilated area and dependent on product/grade combination stored at ambient temperature or in a temperature controlled area that provides spill containment.

The ideal storage area would provide impervious containment that exceeds the contents of a single drum. Drums on suitable pallets may be stacked. The storage area must comply with the national / local regulation

Preferably material should be pumped from drums; however, pressure should never be applied as a means of transferring liquid. If the drum will not be completely emptied on a single transfer, it is imperative to prevent atmospheric moisture contamination of the remaining diisocyanate. Even a small amount of contamination by water or other foreign substance could result in excess pressure and catastrophic failure of the drum. Do not reseal a drum if contamination is suspected.

The preferred method for disposing of empty drums is to contract with an approved drum reconditioner. If not reclaimed, the drum must be emptied, thoroughly neutralized, the label removed and the drum crushed to prevent reuse.

4.1.1. Receiving shipment

The labels on the drums must always match the information on the delivery documents.

The owner of the receiving facility must prepare written operating procedures covering all aspects of the unloading of diisocyanates. Specific procedures concerning the division of responsibilities between the driver and the cargo receiver are required. In particular, ensure the following situations have been addressed

- Drums may fall out of container when the container doors are opened
- Inspection of drums to identify any damage or leakages. The type and extent of damage should be recorded on transport/delivery document and countersigned by the driver
- It's recommended not to perform the unloading with a single person, an additional person could provide assistance in the case of spill or incident

The driver has a duty to his (her) employer to protect the integrity of the vehicle; the receiver, to ensure that product is unloaded into the right storage in such a way as to eliminate any risk to people, surroundings, environment and the product. Both must cooperate fully in the discharge process to ensure that it is conducted safely. The SDS of your supplier can be consulted for the relevant Scenario under REACH with respect to loading and unloading of diisocyanates including handling packaging.

4.1.2. Emptying of drums

Proper emptying to ensure that the contents of all drums are fully utilised is the most important aspect of in-plant responsible drum management. It affects cost, regulatory compliance and legal liability. It is therefore strongly recommended to have quality control measures in place to make relevant checks regularly. An "empty drum" is one which is "drip free". This means the drum has been emptied according to the practices commonly employed to remove the diisocyanate from the drum (e.g. pouring, pumping or aspirating). The avoidable residues of valuable diisocyanates left in drums represent lost profits. This is virgin product that has been paid for. On the other hand, costs for residue elimination will increase.

Product labels must not be removed. This is required by EU regulation for any drum formerly containing diisocyanate. These labels are required to communicate all necessary safety/hazard information to each person handling a full or an emptied drum which may contain residues.

Emptied drums should be closed tightly with all plugs in place and externally clean. They should be stored in a bunded area under cover to remain dry.

It is important to note that the recommendations to empty, decontaminate, refit bungs and store under cover are essential to the safe management of used diisocyanate drums. Should proper emptying or decontamination not take place, or moisture is present in the drum, then a build-up of internal pressure may take place. Empty drums should be visually inspected on a regular basis for signs of any pressure build-up. If pressure build-up is noticed, the operator wearing PPE would have to carefully release one of the bungs to allow venting but NOT so far so that the bung ejects with force from the lid.

4.1.3. Emptying procedures

At the final emptying phase with ordinary pumps, the back flows from the dip tube together with the remaining product on the bottom and side walls of the drum result in 1 to 5 litres of residue. This quantity of hazardous material is too large to assure safe and complete decontamination. A possibility to reduce the residual content is the use of pumps equipped with a non return valve at the bottom of the dip tube. Depending on the individual product, its temperature and viscosity, a residual content of 400 to 1000 g can be achieved.

4.1.4. Heating drums of Diisocyanate

Occasionally diisocyanates must be heated to aid the transfer of material from the drum. The following are intended to be guidelines for safely heating drums of diisocyanate. Each situation may be different depending on the equipment and expertise available at the facility.

- Ensure both the ¾-inch and 2-inch bungs are wrench tight. Diisocyanates will react with moisture, even atmospheric moisture, to form carbon dioxide gas that could result in a dangerous pressure build-up in the drum(s). Do not place drums in a water bath or steam cabinet. Place drum(s) in a warm area or hot room that will provide a consistent, even temperature above the freezing point. The time it takes to heat diisocyanates depends on the temperature of the area/room, the heat source and air circulation.
- Electric heating devices intended to be affixed to the outside of the drum(s) are not recommended because they result in localized heating of the material and could increase dimer formation. Instead a heating cabinet could be used. Drums should be placed on pallets to allow good circulation of the hot air. Pallets should be equable placed in the heating cabinet to allow maximum heating result.
- Induction heating units for individual drums are energy efficient and do not have high contact temperatures, melting of diisocyanates requires less melting time than in standard heating cabinets.
- Overheated drums may lead to uncontrolled chemical auto reaction and even development of fire. The maximum temperature setting for drums placed in a heating cabinet should not exceed 80 °C. For IBCs the maximum is 60°C due to the packaging material.
- Because diisocyanates are comprised of isomers with slightly different freezing points, it is recommended the material be agitated after heating to ensure it is not only thoroughly heated, but also thoroughly mixed. This can be accomplished without opening the drum by using a drum roller. If the bung must be removed to mix the product by mechanical means after heating, proper ventilation will be required and the personal protective equipment as specified in chapter 3.1 must be worn.
- Monitor the drum(s) for any abnormalities during melting, particularly swelling. Should any abnormality be observed, discontinue heating immediately. Bulging drums are potentially dangerous and must be handled only by trained personnel.
- After heating, wipe any moisture from the top of the drum(s) prior to opening. Move the drum(s) to a ventilated area and - wearing the proper personal protective equipment - open the bung slowly to relieve any pressure build-up that may have occurred during the heating process.

4.2. Intermediate Bulk Containers (IBCs) (MDI only)

MDI can be shipped in Intermediate Bulk Containers (IBCs). They have a capacity of ~ 1,000 litres and are constructed of high density polyethylene housed within a steel cage for protection of the inner bottle. The bottom discharge on these containers is a 2-inch male Camlock® coupling with closure cap. The top fill opening is a standard 6-inch threaded fitting with closure cap. Reference to Appendix 2. These containers should be stored in a dry environment that will maintain the temperature of the material above the freezing point. Consult the specific product MSDS for recommended storage temperature range and product shelf life. The storage area must protect the containers from physical damage that could result in a leak/spill. The ideal storage area would provide impervious containment that exceeds the contents of a single intermediate bulk container and must comply with local regulations.

The use of IBCs for toxic material Class 6.1, PG I is forbidden. Although TDI is classified as Class 6.1, PG II **it is highly recommended that IBCs are NOT to be used for TDI transport/storage**. The ISOPA members only move TDI in either bulk equipment or drums. Reason for not using IBCs for TDI is the quantity spilled in case of a product spill as a result of a puncture or otherwise.

4.2.1. Receiving shipment

The IBC numbers (if any) should be compared with and always match the numbers on the delivery documents.

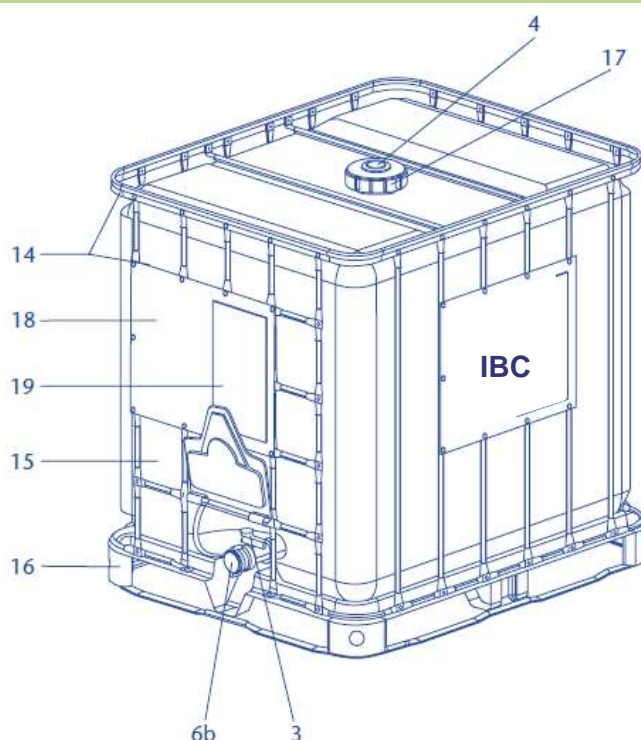
The IBCs should be examined using the checklist for any transit damage and to ensure the integrity of outlet fittings, vents and any seals. The type and extent of any damage or defect should be recorded on the delivery documents and counter-signed by the carrier (driver).

If there is a visible leak from the IBC the appropriate emergency response procedure must be immediately activated.

The type and extent of any damage or defect should be recorded on the delivery documents and countersigned by the delivery agent.

Checklists for receiving Intermediate Bulk Containers (IBCs)

IBC number:		Comments	
		Yes	No
14	Is frame damaged ?		
15	Is tank damaged ?		
3	Is discharge valve closed ?		
16	Is pallet damaged ?		
6b	Is protective cap sealed ?		
17	Is lid sealed ?		
4	Is bung sealed ?		
18	Is transport/product labelling correct?		
19	Does labelling match delivery documents?		



4.2.2. Emptying IBCs

Before emptying

Before proceeding to discharge, remove the bung (4) to prevent any vacuum damage the air flow has to be identical to the liquid flow. (see drawings,) Remove the protective cap (6b) from the outlet fitting (6a) and any manufacturer's seal. Remove the plug from the coupling of the receiving plant's emptying equipment. Connect the coupling to the outlet fitting (6a).

Open the discharge valve (3).

After emptying

Once the IBC has been emptied completely close the discharge valve (3). Disconnect the coupling of the receiving plant's emptying equipment, clean the outlet fitting (6a) and immediately replace the protective cap (6b). It is recommended that the protective cap (6b) is also resealed. Replace the bung (4)

Replace the plug on the coupling of the receiving plant's emptying equipment.

4.2.3. Re-use of IBC

A Single trip

Where it is agreed in advance that the IBC is to be used for a single trip only, then it is the customers responsibility to ensure the container is emptied to drip-free state and to arrange for disposal. Disposal should be arranged through an IBC manufacturers own recycling system or with an approved and audited reconditioner or recycler.

B Multi trip

Where the IBC is intended for refilling after drip-free emptying it should be externally clean and correctly labelled. The product supplier must then be contacted to arrange return shipment or otherwise.

C Reuse, recovery or disposal update to current way of working

It is strongly recommended that composite IBCs are used as a multiway package. Nevertheless in certain cases the distance required for container return may make this proposition uneconomic or the container itself may be damaged and not suitable for return.

It should be confirmed in advance whether the IBC is intended to be returned for reuse (whereby collection will be arranged by the product supplier) or whether safe and correct disposal is the responsibility of the customer.

D Disposal

Recycling or disposal of all plastic or chemical waste must be done in accordance with national regulations and a certificate should be received. Recycling and disposal systems should be covered by written procedures, verifiable records and auditing of contractors.

4.3. Cleaning of spillages (small / large)

Spills involving MDI or TDI require immediate response by trained, knowledgeable personnel. Personnel who are not trained must leave the area immediately and notify the appropriate emergency response personnel. If assistance is needed, call the 24/7 emergency response number of the supplier.

Spillage or leakage:

- Always wear personal protective equipment (PPE)- see section 3.1
- Do not breathe fumes or vapor.
- If possible without personal risk, try to prevent contamination of soil and water.
- When outside in the open air, evacuate the area ensuring personnel are up wind
- If in a confined space, ventilate contaminated area thoroughly.
- Contain or cover the spillage.

Any spillage should be contained as quickly as possible. Bunds to restrict the area may be made of sand, earth or any other containment material. Shallow containers should be used to collect any product still being discharged. Try to prevent product entering any drainage systems. Diisocyanates will react with water and form insoluble polyureas thus blocking drainage systems. If material enters drainage system it should be pumped out into open vessels at the earliest possible stage.

In case of damaged or leaking drums or IBCs, it is essential that suitable precautions are taken and strictly adhered to. The leakage may be contained by sealing and/or placing the packaging in a position, where the puncture is in uppermost position to prevent product loss. Replacement IBCs, new drums or oversized drums should be provided for leaking packages.

Minor punctures may be sealed by the use of wedges, gaskets, cushions of resistant materials, notably wood, PTFE or neoprene rubber.

Once the product has been contained and safely transferred, all absorbent material and any decontaminants should be collected into open top drums. Drums should be removed to a site for safe disposal after the chemical reaction is finished.

Neutralise the affected surface with liquid decontaminant and test the atmosphere for residual Diisocyanate vapours. Re-establish the area as safe for use.

Absorbents

- Mineral agent
- Sand
- Oilsorb
- Vermiculite

Decontaminating Liquid:

Sodium Carbonate	5 – 10 %.
Liquid Detergent	0.2 – 2 %
Water	to make up to 100%

Special equipment for dealing with drums and IBCs

- Oversized drums fitted with a top valve for venting .If the oversized drums have to be transported they have to be approved for transportation of dangerous goods
- Spike for puncturing bulging drums

For Intermediate Bulk Containers (IBCs) careful inspection should be made of discharge valves, lids, loading points and seams. If there is no visible damage to these components and the pallet is in proper condition, the container can be used for the continuation of shipment.

5. Storage

5.1. General information

- The handling of IBCs / drums should only be carried out using fork-lift trucks with a fork arm length of at least 1.20 metres. Accordingly, only lifting equipment with a safe holding device should be used.
- The number of drums or IBCs that can be stacked on top of each other must comply with the characteristics of drums or IBCs (Refer to technical specifications) .
Typical value : 2 IBCs - 3 Drums
- During storage all relevant regulations and the information from the safety data sheet must be observed. IBCs / drums when stored should be under cover and within a bunded area meeting legal requirement or sufficiently large enough to contain the content of at least one IBC / drum or 10% of the overall storage amount, which ever is more stringent.
- If there is a visible leak from the IBC / drum, the appropriate emergency response procedure must be immediately activated.
- Salvage packagings shall additionally be marked with the word "SALVAGE".

5.2. Seveso Directive (European Directive on the Major Accident Hazards)

In 1982 the first Directive on the Major Accident Hazards of Certain Industrial Activities (82/501/EEC) was adopted. It has been updated a few times since then, and is generally known as the "Seveso Directive". It provides the members of the European Community with uniform rules for:

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

This Council Directive in its currently valid version is of importance to all members of the polyurethane industry who process and store TDI in quantities above defined limit which is currently 10 tonnes.

The Directive only applies to EU member states, but could be superseded by national legislation. Non EU-States could also decide to implement a similar approach.

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

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

National / Local legislation

The consignee should ensure that national and/or local requirements are met e.g. local permits to handle and store toxic substances / preparations.

5.3. Storage requirements**Segregation**

There are legislative requirements for hazard segregation in storages facilities. These requirements could differ per country. However it is recommended to always keep diisocyanates segregated from foodstuff. It is also recommended to keep diisocyanates away from oxidising, corrosive or flammable materials.

Temperature

Temperature in storages of diisocyanates must be within the range as specified in the technical information documents from the supplier, typically ambient. Except for monomeric MDI,TDI 100% and 95% 2.4 isomer the storage temperature will be > 20 °C. If products are stored outside the temperature ranges as specified by the supplier then the quality of the product could deteriorate.

Moisture

Packaging must be stored tightly closed due to the risk of reaction with moisture / water. Therefore it is strongly advised to store packagings inside a building and not in the open air.

6. Responsible management of empty diisocyanate steel drums

6.1. Emptying of residues

All drums should be drained at a temperature between 20°C and 30°C for about 2-3 hours. For monomeric MDI, the drums should be drained at a temperature between 45°C and 60°C. Because of the potential hazardous vapours it is of utmost importance that this is being done in a well ventilated area wearing the correct PPE.

Option 1

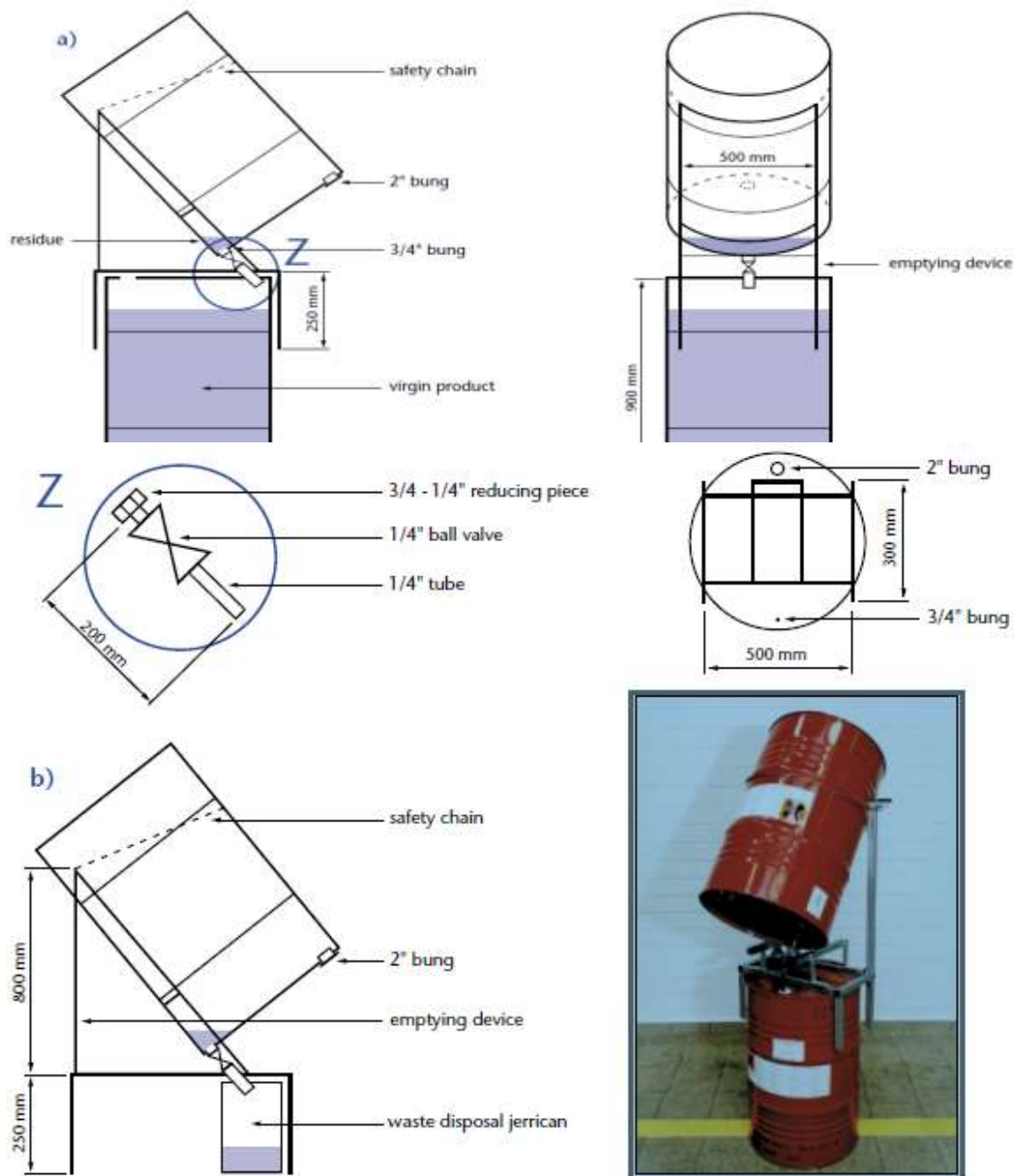
For this emptying procedure it is helpful to make use of a drum emptying device to secure the drum in an appropriate position as shown in the drawing below.

In combination with a suitable reducing piece combined with a tube and a ball valve it allows a proper emptying of the residues into a drum with usable material or directly in a waste disposal jerrican as desired. This reducing piece should be screwed into the bunghole of the drum being emptied and connected directly into a modified bung ensuring a tight fit to prevent emission of vapour of the receiving drum or jerrican. This applies to MDI, but is especially important for TDI. After emptying the drum, the ball valve should be closed, the drum turned back, the reducing piece removed and the bunghole closed.

Emptying of TDI/MDI drums through 3/4" or 2" bunghole into

a) drums with usable product or

b) waste disposal jerricans (5-60 ltr.) or drums

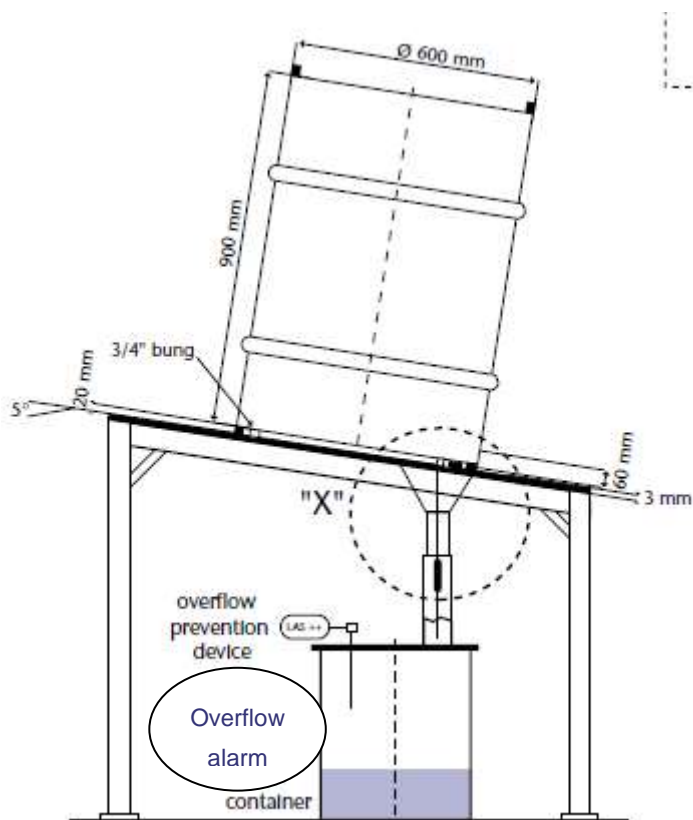
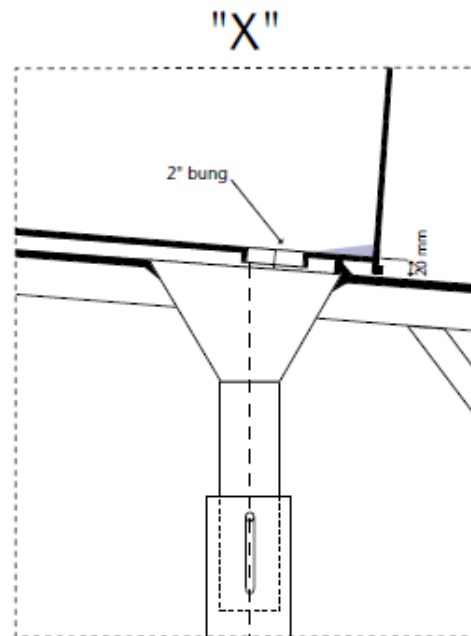
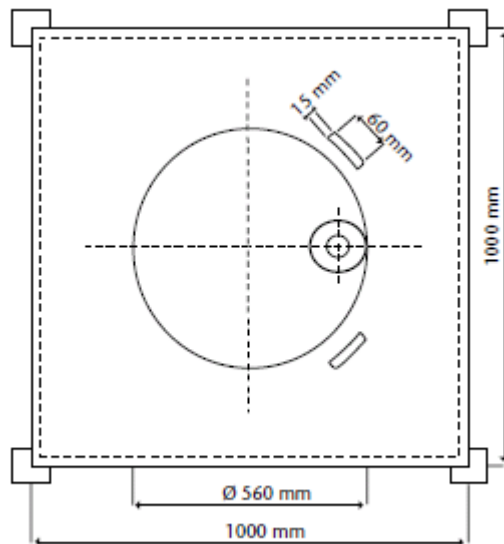


Option 2

Another method to reduce vapour release during draining is to use a sloped platform provided with a protruding ring to allow a central positioning of the drum and a funnel for the reception of the diisocyanate as shown in the drawing below. If there are larger quantities of residues they should be poured directly into the funnel before the drum is placed on the ring, the bunghole always well positioned above the funnel. The nearly tight contact between the ring and the open side of the drum prevents emission of diisocyanate vapours during the draining of the diisocyanate residues into the receiving vessel via the funnel. After the emptying, the drum should be turned back and the bunghole closed. In order to avoid diisocyanate vapour emission, the ring should be

covered by a lid if no drum is in place. To avoid spillage, the process should be well monitored and an overflow alarm could be considered.

Emptying of TDI/MDI drums through 2" bunghole into waste disposal container (5-60 ltr.) or drums



6.2. Emptying of residues

Introduction

Evacuation of any residues and appropriate temperature are of essential importance for successful decontamination. Special attention should be given to the temperature at the bottom of the drum. Storing the drums to be decontaminated on a wooden pallet will have a positive effect as the temperature on the bottom of the drum and the product temperature will be higher than if placed directly to the ground.

The decontamination of monomeric MDI must be effected in a heating cabinet at a temperature between 45°C and 60°C.

Diisocyanates presenting a viscosity of more than 150 mPas (PMDI, prepolymers) require a temperature between 25°C and 30°C.

A temperature between 20°C and 25°C is sufficient for the remaining diisocyanates except for 100 % and 95% 2,4 TDI for which the recommended temperature is 30°C as the freezing point is 22°C.

Drums must also have been stored upright for at least two hours before proceeding to allow product to drain from the drum wall to the bottom.

The preferred method is the one involving sodium carbonate as a decontamination product which is reusable

Method

For the decontamination of one drum two liters of a decontamination product is required consisting of 5 to 10% sodium carbonate and 0.2% to 2% of liquid soap in water.

The decontamination process

The following steps should be taken:

- Step 1** The operator must be wearing PPE as detailed in section 3.1.
- Step 2** Preparation of the decontamination solution as mentioned above.
- Step 3** Check if the drum is really drained and empty by weighing.
Opening of the drum:
Cautiously open the 2" bung of the drum which has been emptied by draining after having assured adequate ventilation. A slight internal pressure may be present in the drum as a result of thermal fluctuations.
- Step 4** Pour 5 liters of the decontamination solution into the drum, unless the drum still contains more than 1 liter of product.
- Step 5** Rolling of the drum:
Close the bunghole firmly, place the drum on its side and roll it at least four times, place it upside down for a moment and turn it again to its upright position.
- Step 6** Reopening of the drum:
A slight overpressure will occur in the drum due to the chemical reaction which has started. Release the 2" bung without removing it to prevent any pressure build-up¹.
- Step 7** Repeat step 5 and 6
- Step 8** After two hours repeat steps 5 and 6 three times
- Step 9** After one day, mix the solid with the liquid inside the drum thoroughly.
- Step 10** Repeat step 9 the next two days (drum should be stored at temperatures > 20 °C to ensure complete reaction).
- Step 11** Decant liquid and separate from the solid. The liquid shall be stored in an extra drum and is to be used for the decontamination of the next drum².
- Step 12** Leave the drum under cover to stand for at least one week.
Notice that the reuse of drums is not recommended , especially for non industrial usage

¹ Don't leave drum closed for more than only a few minutes, otherwise the pressure-build up may rupture the drum.

² Be careful! The liquid contains traces of TDA (Toluenediamine), which is a cat 2 carcinogen. TDA decays slowly in the presence of air and sunlight.

The drum content

The different diisocyanate residues are converted by the corresponding decontaminant solution into harmless polyurea / polyurethane compounds and carbon dioxide gas. These may remain in the drum together with the residual decontaminant solution and will be collected by the drum reconditioner / recycler.

Identification of the decontaminated drums

After decontamination, it is strongly recommended to identify the drums in order to enable the forwarder, the reconditioner or recycler to recognize them as decontaminated.

7. Recommended packaging

All packaging for TDI must be UN-approved. It is ISOPA's recommendation to also use UN-approved packaging for MDI.

7.1. Drum specifications

It is expressly noted that it is the producer's responsibility to select the appropriate packaging based upon all information at their disposal including the specific application, regulatory compliance, product compatibility and shipping requirements. The UN states that TDI may be transported in a package having an UN mark of group II which is Y. For safety reasons the most common mark to use is X 1.2/250. MDI can be transported in package Z, group III but for safety reasons the recommendation is to stay on the X 1.2/250.

The minimum performances must be

- Air tight pressure of 30 kPa
- Liquid tight to pressure of 250 kPa
- Liquid tight after drop from 1.8 m (1.5 x 1.2)
- No plastic deformation after stacking filled drums 3 high

Reconditioned drums cannot be used

It is also recommended to use

- Double washer for octagon thread
- Drums that have passed successfully Helium test

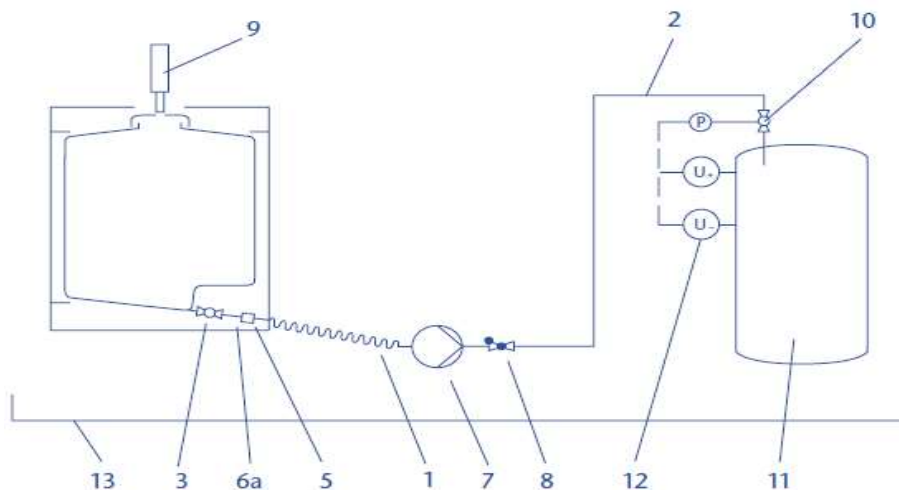
7.2. Guidelines for the design of composite IBCs for polymeric MDI and derivatives and for base, blended and formulated polyols

See Appendix 2

7.3. Product transfer system recommendations for IBC

Emptying is best done in such a way that migration of moisture, skin contact with the product and inhalation of its vapours are avoided.

This is best done using a tight pump system with standardised 2 inch bottom discharge.



1	Outlet hose
2	Filling line
3	Discharge valve
4	Bung
5	Hose coupling, female section
6a	Outlet fitting, male section
6b	Protective cap
7	Pump
8	Non-return valve
9	Desiccant cartridge (optional)
10	Shut-off-valve
11	Machine tank
12	Level sensor
13	Containment basin

In the drawing above describes the way by which the product can be transferred directly to the machine tanks. Illustrated below is such a suitable transfer system: the bung (4) has been replaced by a desiccant cartridge (9) and the protective cap (6b) removed.

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

In many European countries, National Emergency Response Schemes for hazardous materials exist. Such schemes must take precedence over any advice given in this chapter. Furthermore, a Europe-wide Emergency Response System organised by CEFIC (Intervention in Chemical transport Emergencies = 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.

8.1. Purpose and Scope

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

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

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

8.2. Preparedness and Emergency Advice Requirements

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

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

8.3. Contractual Liabilities

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

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

8.4. Technical Communication

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

- Prepare and maintain an Emergency Response Manual based on the principles described in Section 8.3
- Ensure that the training and equipment at participating centres is adequate
- Agree on common methods of approach in the resolution of transport emergency situations

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

8.5. Use of the Mutual Aid Scheme

The essentials of this scheme are as follows:

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

- people
- property
- the environment

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

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

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

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

9. Transport Equipment Specifications

9.1. General

The specifications for transport equipment are standardised as described in the related ECTA / CEFIC *Guidelines for Transport Equipment used for Chemical Packed Cargo* <http://www.cefic.org>

The specifications in this chapter include transport vehicles, trailers and containers used for the carriage of packed cargo by road or intermodal transport.

All contracted logistics service providers will be held responsible and accountable for presenting their equipment for loading of packed products in compliance with international legislation (e.g. ADR & IMDG), national legislation for domestic transportation where this applies, and legal restrictions re. foodstuff / food grade transport in combination with chemicals (combined loads of chemicals and foodstuffs in the same loading space is not allowed)

Additional guidance on the roles and tasks for load securing are included in the CEFIC/ECTA *Behaviour Based Safety Safe Loading and Unloading* . See: <http://www.cefic.org>

Further guidance on cargo securing can also be found in the *European Best Practice Guidelines on Cargo Securing for Road Transport*, issued by the European Commission - Directorate General for Energy and Transport.

See:

http://ec.europa.eu/transport/road_safety/vehicles/doc/cargo_securing_guidelines_en.pdf

9.2. “Fit for loading and unloading”

The logistics service provider is responsible for presenting the equipment fit for loading i.e.

- in accordance with the ECTA / CEFIC specifications and all legal requirements;
- the floor (plus sides/roof when applicable) must be smooth and free of objects (e.g. protruding nails).
- the loading space must structurally be in sound condition (e.g. watertight - no holes).
- a visual inspection must take place prior to entering the transport unit if floor is free of “holes”. The floor construction must allow the weight of fork-lift trucks when entering the loading space.
- the floor must be of a material to prevent slip or trip hazards (incl. at door entrance).
- clean, dry, odour-free;
- suitable for the product to be loaded.

Transport equipment

The following general specifications apply:

- with proper and functioning cargo securement systems;
- with the necessary legally required orange-coloured plates for transport of hazardous goods.
- the floor must be sized to allow lateral stuffing of 4 drums (Ø 58.5 cm) without overlapping seams.
- all equipment should be sealable and easy to lock tightly from ground level.
- sufficient (sunken) lashing points must be attached to the actual transport unit to enable proper securing of cargo.
- equipment for load securement must meet national and international requirements.

Note:

The specifications in this section are primarily applicable to transport equipment. There exist product specific requirements i.e. compatibility, heating, cooling, stacking etc., which are detailed in the contract agreements between parties.

9.3. Different Types of Transport Equipment in Use

9.3.1. Vehicles with sideboards constructed according to EN 12642 Code L (Tilt trailers or so called “L”-trailers)



Tilt trailers are trailers with tarpaulins on both sides and with sideboards which are fixed to the floor frame and can be tilted in order to allow loading and unloading from both sides as well as from the back. The dimensions are in general as follows: 13,60 m length and 2,44 m internal width.

9.3.2. Vehicles without sideboards constructed according to EN 12642 Code L (curtainsider or “tautliner”)

A curtainsider is based on the same construction as the tilt trailer but without sideboards fixed to the floor frame. Its tarpaulin sides can be moved easily by pushing them aside like a curtain. The tarpaulin is meant to protect the cargo against weather conditions, but is not suitable for cargo securing.

9.3.3. Vehicles constructed according to EN 12642 Code XL

EN 12642 Code XL refers to reinforced body structures as described in the revised standard EN 12642:2007. Vehicles constructed according to the revised standard EN 12642 Code XL need to fulfill certain minimum requirements regarding stability criteria and test conditions of the front wall, rear wall and side walls. Vehicle body structures in compliance with the requirements of this standard have a certificate and are in general marked with a specific sign.



9.3.4. Box trailers

Box trailers do not have flexible tarpaulin sides but are completely surrounded by a stable metal or steel construction. The closed unit offers improved stability and cargo securing for different types of packaging. Because its sides cannot be opened, only loading and unloading from the back of the vehicle is possible. This requires a fixed ramp or a movable ramp ('loading bridge') for the cargo to be moved in or out of the box trailer

9.3.5. Temperature controlled trailers



Temperature controlled trailers do not have flexible tarpaulin sides but are completely surrounded by a stable metal or steel construction whereby the walls are insulated and are designed to transport goods under a certain temperature. The trailer is equipped with an aggregate allowing to set temperatures between plus and minus

25 °C. Possibilities for load securing are limited due to the structure of floor and walls.

9.3.6. Swap bodies

Swap bodies have nearly the same constructional characteristics as the above described five vehicle types, but need to be put on a chassis for any kind of movement. They are typically used for intermodal transport and drop and swap operations.

9.3.7. Containers

ISO containers have a solid closed construction as defined in ISO standards (e.g. ISO 830 and ISO 1496-1) including requirements such as:

- a rigid construction for repeated use, trans-loading and terminal operations;
- a design to facilitate the carriage of goods by one or more means of transport;
- fittings permitting its easy stowage, handling and stacking.

ISO containers with a length of 20 or 40 foot and an internal width of 2,34 m are most used. In addition there are 40 and 45 foot containers with an inner width of 2,44 m (pallet wide) which are not constructed according to an ISO standard.

Appendix 1:

Chemistry of the reaction of diisocyanates with water

Reaction of Isocyanate and Water

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

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

Every 250 grams of MDI consumes 18 grams water and produces 25 litre CO_2 gas.

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

Practical Meaning of this Reaction

A small amount of water in drums or IBC will lead to a huge increase in pressure which can exceed the maximum available pressure with as consequences an explosion of the drum or IBC with projection of piece of metals and leak of product

For example A glass of water (175 ml) in a drum (215 L) of TDI will lead to an extra pressure of 2.5 bars which is the standard Liquid tight pressure for the drums

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

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

When diisocyanates 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 diisocyanate from the water.

Thus, large spills of diisocyanate in water do not react rapidly. Sand or other absorbing materials will disperse the diisocyanate 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 diisocyanate 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 drum or IBC dry and closed to avoid moisture ingress**

Appendix 2:

Recommended typical ISOPA composite IBC design configuration for both the polymeric MDI (PMDI) and derivatives and for base, blended and formulated polyols.

Construction

Dimensions	1000 x 1200 x 1200mm (approx. height)
Top	Must have adequate rigidity to support mounting of stirrer and. to restrict container flexing to a minimum. This is also required to keep the fill opening precisely located. Must be suitably designed for stacking
Metal frame	The plastic container must be adequately protected from mechanical damage. Protection particularly important for outlet valve and container bottom vulnerable to fork-lift damage.
Pallet	Must allow for roller conveyor and four side fork-lifting. Forks in captive slots, shaped bottom plate designed to fully support container.
Bottom	Sloped towards outlet to allow maximum drainage, minimum dead volume. Serviceability of bottom valve.
Volume	1000 litres

Service Equipment

Fill opening	Min. DN 150 mm with lid
Trisure or equivalent in lid	2 inch bung with integrated pressure release including internal swell shield
Bottom discharge	
Connection	2 inch
Valve	2 inch screwable valve, lever securable
Coupling	2 inch Kamlok male and cap for diisocyanates 2 inch screw connection (S60x6) and cap for polyols
Instruction panels	Front panel with paper holder plus 2 additional side panels for labelling and instructions

Material

Tank	HDPE
Frame	Galvanized steel or equivalent in accordance with UN requirements
Pallet	Galvanized steel or equivalent in accordance with UN requirements
Valves	Plastic
Connections	Plastic
Gaskets	Compatible with products

Certification

In accordance with ADR / RID, IMDG code and national regulations for packaging group II or III. Additionally approved for active storage.

Marking

Primary marking	UN 31 HA1/YorZ
Additional marking	In accordance with ADR / RID, IMDG code and national regulations.
Owner's marking	Optional
Container numbering	Optional
Product marking	See chapter 2.2

Screwed 2 inch S60x6



Camlock



DISCLAIMER

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