

GUIDELINES

Emergency Response for Transport of TDI & MDI



FOREWORD

The second edition of the “Emergency Response Manual for Transport of TDI and MDI”, dated October 2003, has been thoroughly reviewed. The intention was to update information to incorporate the changes to the Mutual Aid Emergency Response Scheme as agreed between the ISOPA members companies and insure the coherence with the ICE Scheme (Intervention in Chemical Transport Emergencies) developed by CEFIC.

ISOPA Logistics Team

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1. INTRODUCTION

1.1. PURPOSE

This manual has been prepared by ISOPA, the European diisocyanates and Polyol Producers Association. It is designed to augment and strengthen existing National and Company communication systems when dealing with TDI and MDI and to complement the ICE Scheme. It describes a mutual aid scheme whereby ISOPA companies have undertaken to respond as necessary on each other's behalf in order to ensure that expert assistance is available as quickly as possible at the scene of a transport emergency involving TDI or MDI.

1.2. ADOPTION

All ISOPA member companies have signed the convention for providing mutual aid in the case of incidents during the transport of TDI and MDI. ISOPA will review and update (if necessary) this document every two years or whenever there are major changes or new experience or knowledge becomes available, whichever occurs first. ISOPA recommends that all parties active in the transportation and distribution of diisocyanates, consider to adopt these guidelines in order to be prepared in case of an incident.

1.3. MDI/TDI PRODUCTS

Toluene Diisocyanate (TDI) is classified and regulated as hazardous for handling and transport. The "UN Sub-committee of Experts on Transport of Dangerous Goods" decided in July 1994 to remove Diphenylmethane Diisocyanate (MDI) from the list of hazardous goods. However, MDI continues, quite properly, to be regulated in EU countries as hazardous material in handling and usage. For this reason it has been decided to continue to maintain MDI in the Emergency Response System. To avoid the need for repeated explanations in this document, wherever MDI is referred to as a dangerous good for transportation it should be understood in this sense. Properties, hazards and safety information for TDI and MDI is attached (see Annex 2).

1.4. INTEGRATION WITH ICE

1.4.1. Definition

ICE: Intervention in Chemical Transport Emergencies: CEFIC co-operative program in the event of an incident during the transport of goods to provide information, practical help and appropriate equipment to the competent emergency authorities.

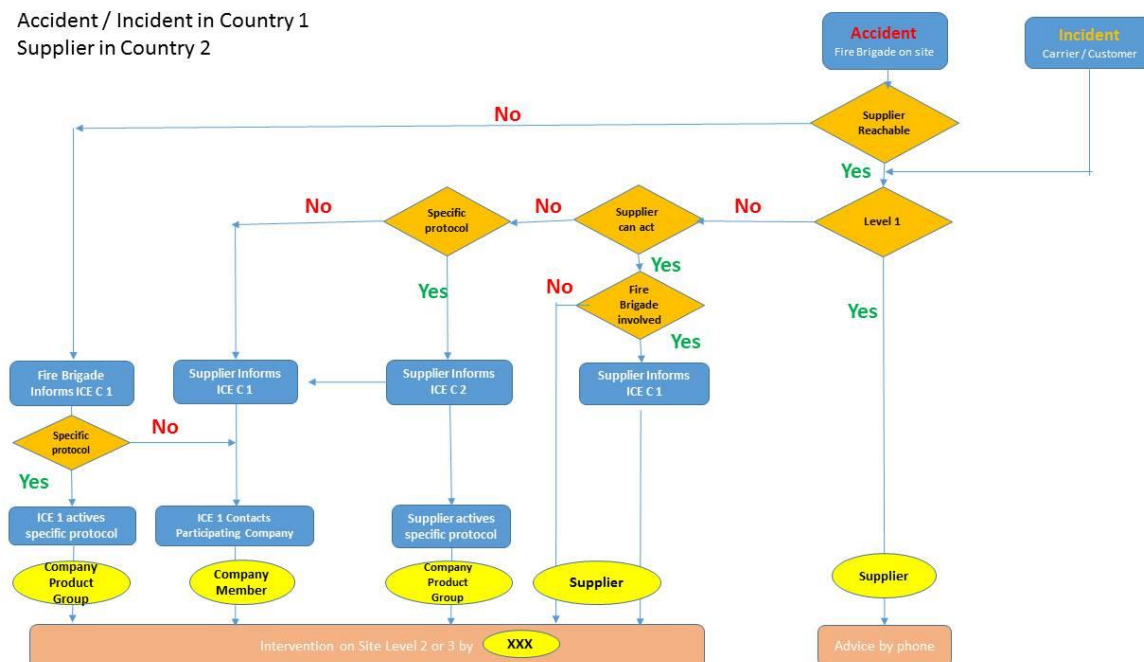
Participating Company /Company Member: Company who is member of ICE Scheme (TUIS, Transaid ,...)

Company Product Group: Company who has signed a specific protocol

Specific Protocols (Mutual Aid Scheme) : Diisocyanates (ISOPA) , Titanium Tetrachloride , Bromine , Ethylene Oxide

1.4.2. Flow Chart

Accident / Incident in Country 1
Supplier in Country 2



The chart illustrates the typical flow of information in case of accident on site or during transportation of dangerous goods.

In such a case, the fire department can need assistance (advice by phone or on site or response on site) from chemical industry experts. This assistance can be done using the ICE scheme (normally only for distribution incident) or a specific protocol as the ISOPA mutual aid protocol.

When an expert cannot be found in the country, the ICE national center can contact other ICE national centers in Europe to obtain information or assistance.

If ICE scheme and ISOPA mutual aid protocol (= specific protocol) are activated in parallel, it is important to implement a good communication between all parties involved (ICE National centers, ICE responders, Supplier and ISOPA Company responding).

1.5. INTERPRETATION CAVEAT

The prime responsibility for dealing with transport emergencies involving chemical and particularly dangerous goods rests with the national emergency services in the country concerned. Nevertheless, emergency services in many European countries (see annex 8) recognize that the chemical industry can provide a vital supporting role and therefore seek their expert advice and assistance on safe methods of handling, recovery and disposal of chemicals involved in transport emergencies. The chemical company contacted for advice or assistance may be the manufacturer, supplier, importer or user of the chemicals, or may be selected for other reasons, for example, proximity to the scene of the emergency.

The ISOPA mutual aid scheme can be activated on its own or can complement the ICE scheme (see Annexes 4 and 8). It is the individual responsibility of users of this manual to evaluate and apply it while fully taking into account all specific circumstances and their own situation.

No part of this manual should be used or interpreted in a way which would conflict with existing international and/or national legislation, including competition law. In any case, applicable legal provision will always take precedence over any part of this manual.

2. THE MUTUAL AID SCHEME

1. The European Diisocyanate and Polyol producers who are members of ISOPA have established a system of mutual aid to deal with potential emergencies arising during the transportation of Toluene Diisocyanate, Diphenylmethane Diisocyanate or their derivatives in Europe.

2. The principles of the resulting “Convention for providing mutual aid in the case of incidents during the transport of TDI or MDI” are as follows:

a) In the event of any difficulty occurring during transportation of a shipment of either TDI (UN- Number 2078) or MDI or their derivatives forwarded by one of the participating COMPANIES (meaning ISOPA member Companies), such difficulty, in the supplier’s opinion, having the possibility to cause damage to persons, property or the environment or preventing the safe continuation of transportation, then the said COMPANY may request another COMPANY closer to the scene of the incident to intervene.

b) In this context, “transportation” is taken to mean all of the activities associated with the transport unit, including unloading.

c) All COMPANIES will promptly respond to a request from another COMPANY which considers that there is a need for technical advice or assistance at the scene of the incident.

d) The request for any intervention at the scene of the incident may be made by telephone but must be confirmed in writing or by email.

e) Each of the COMPANIES may be requested to provide assistance from an appropriate Emergency Response Centre. The contact numbers are listed in Annex 8.

f) The COMPANIES undertake to assist each other as far as is possible. The role of the intervening COMPANIES is to provide technical advice to the Emergency Authorities on the nature of the product and on the measures necessary to deal with the incident, and to provide technical assistance if requested by the Emergency Authorities.

g) A company which has asked another COMPANY to send staff to the scene of an incident remains responsible for the support given to the Authorities. The intervening COMPANY acts on behalf of the requesting COMPANY until a representative of the latter reaches the scene or until advised by the requesting COMPANY that they may withdraw.

h) The intervening COMPANY will use its best efforts to keep the requesting COMPANY informed of progress.

i) If asked by the requesting COMPANY, the intervening COMPANY and their equipment should be prepared to stay at the scene unless otherwise agreed between the requesting COMPANY and the intervening COMPANY. In any incident, where the Emergency Authorities are not involved, the intervention will be restricted to limiting any danger and to stabilizing the situation pending arrival at the scene of a representative of the requesting COMPANY.

j) If the Emergency Authorities in any country call for assistance from a company under the provisions of a formally binding national scheme, then the provisions of that scheme will be paramount. In such circumstances, the intervening COMPANY shall promptly advise the requesting COMPANY.

k) In the event of “force majeure” the obligations of the Convention are removed but the intervening COMPANY should inform the requesting COMPANY of the event of the “force

majeure” as soon as possible. For the purpose of this clause “force majeure” means any cause beyond the reasonable control of the intervening COMPANY.

l) In the case of intervention the intervening COMPANY will be reimbursed as soon as possible by the requesting COMPANY for all expenses so incurred during working and travelling from the location of the intervening COMPANY.

m) The intervening COMPANY shall have no liability or responsibility for any damages suffered by the requesting COMPANY or a third party, and the requesting COMPANY shall indemnify the intervening COMPANY accordingly.

n) Each member company takes on responsibility, , for organizing the diisocyanate emergency response provided for in the ISOPA ER Convention. The COMPANY establishes, a 24 hr manned English spoken emergency response center phone number (see Annex 9)

o) The Mutual Aid Scheme is being integrated with the ICE scheme (see Annex 4), but it can also be activated as a stand-alone product mutual aid scheme.

3. THE EMERGENCY RESPONSE SYSTEM

3.1. INTRODUCTION

The initial advice of the existence of a transport emergency or transport incident involving either TDI or MDI will normally be made by the driver of the transport unit. This will usually be as a result of a telephone call to emergency services. If the driver is unable to contact the emergency services, the initial advice may well be received from a member of the public. It is recognised that the public emergency services may act in one of two ways. Either they may initiate a national transport emergency system which may rely upon the provision of expert advice concerning TDI and MDI from a nominated chemical Company within the system, or they may decide to contact the supplier, whose name and address appears on the consignment notes. In the latter case, the supplier is then able to initiate, if appropriate, the ISOPA Mutual Aid Scheme for assistance in dealing with transport emergencies, as described in Section 2. National schemes may not respond to MDI incidents since it has been declassified.

3.2. LEVEL OF ACTIVITY

It is envisaged that three possible levels of professional assistance could be made available. These are :

- Level 1 Advice by telephone
- Level 2 Advice by experts at the scene of the incident
- Level 3 Active help and provision of equipment at the scene of the incident

3.3. INITIATING THE MUTUAL AID SCHEME

In the event of an ISOPA member COMPANY requesting intervention by another ISOPA member, the following procedures shall apply:

- a) the request for intervention shall be made by the most efficient communication.
- b) the request for intervention shall subsequently be rapidly confirmed in writing by fax or e-mail with heading "ISOPA MUTUAL AID SYSTEM/RUSH TO DESK".

3.4. REQUIREMENTS OF THE INTERVENING COMPANIES

- a) Each intervening Company in the Mutual Aid Scheme should provide persons capable of advising on how to deal with an MDI or TDI incident.
- b) All assistance will be available 24 hours a day throughout the year unless indicated otherwise.
- c) It is the responsibility of all Companies to notify the other Companies of any changes in telephone numbers. A current list with telephone numbers is shown in Annex 9.
- d) All intervening Companies shall ensure that adequate training is given to staff who may be required to attend MDI and TDI transport incidents.
- e) Appropriate equipment for dealing with MDI and TDI transport emergencies for level 3 response (see Annex 5) should be provided by and be available at all intervening Companies (own or contractor equipment).
- f) The responsibility for dealing with the media rests with the requesting Company. Intervention teams should, in principle, not comment to the media regarding product specific information, but should instead refer them to the Company media expert of the requesting Company.

4. GUIDELINES FOR DEALING WITH MDI AND TDI INCIDENTS

Any incident will be a unique situation and it is not possible to write guidelines to cover all eventualities. However, in order to provide the most effective response and minimize the impact of an incident, it is essential to have some procedures established to enable the best course of action to be speedily determined. In transport, TDI is classified as toxic and MDI is unclassified and thus non hazardous. In the EC classification system, for practical purposes TDI is toxic and MDI harmful. The major concerns in any incident are to contain any spillage and to evacuate non-essential personnel and the general public from the area, making sure they are located up wind of the incident location.

There may be language difficulties in certain circumstances and where this applies communications should preferably be in English.

- Name, status and telephone number of the person reporting the incident.
- Location of incident - Description of area (populated area?).
- Have the emergency authorities been notified?
- Is the driver in attendance and providing or capable of providing assistance?
- Is anyone injured?
- Is it a bulk road vehicle, ISOtank, rail tank car or an IBC or drum?
- Are there any signs of product leakage and, if so, from where?
- Is there a risk of pollution?
- If it is a bulk consignment, is the vehicle placarded - what are the details (i.e. numbers on the orange plate)?
- If in IBCs or drums, what details have been noted from the labels?
- What is the name of the company/haulier involved - registration number of vehicle/tank?
- Is the bulk tank or package(s) upright?
- Any other relevant information - current status of the incident.

4.1. RECORDING OF INFORMATION/ USE OF A CALL SHEET

The initial communication could come from a variety of sources including a member of the public. In order to ensure details of the incidents are rapidly established in a clear and logical manner, the use of a “call sheet” is recommended which should include the following (a typical example is given in Annex 6).

4.2. LEVEL 1 RESPONSE - ADVICE BY TELEPHONE

The prime sources of information as to how to respond to an incident will be the information in writing as given to the driver and/or the Safety Data Sheets which detail the properties and hazards of TDI and MDI (see Annex 2).

The advice given will be dependent upon the severity of the incident and the current status at the time of notification. It will also depend upon whether the emergency authorities have been notified, their expected arrival time, or whether they are actually present on site. If the incident has occurred on company premises then the appropriate fire or safety personnel should be informed.

A product expert within the company receiving the incident notification should be advised and asked to stand by in case further clarification of the products properties and hazards is required. It is important to stress the following at an early stage:

- Always wear personal protective equipment.
- Do not breathe fumes or vapor.
- If possible without personal risk, try to prevent contamination of soil and water.
- Evacuate the area ensuring personnel and the public are up wind of the site.
- If in a confined space, ventilate contaminated area thoroughly.
- Contain or cover spillage.

Once this initial advise has been given, if it has not already been done, the emergency authorities should be notified if the incident has occurred in a public place.

4.3. LEVEL 2 RESPONSE - ADVICE BY EXPERTS AT THE SCENE

The provision of either product, transport or fire and safety responders from a company will usually be at the request of the emergency authorities. This may also occur if the incident happened on company premises and further assistance than level 1 - advice by telephone - is required. At an incident where the emergency authorities are present they are in charge of the incident. It is in this context that the company expert(s) in attendance should place themselves at their disposal and any actions undertaken should be at the instruction of emergency authorities.

Under no circumstances should bulk tanks, or drums or any other packaging, that have been subject to a transport incident, be inspected by any person not wearing the personal protective equipment, as specified in the Annex 5 (section 1), for the product involved.

4.3.1 ASSESSMENT – NO VISIBLE DAMAGE

If there is no visible damage to a bulk road vehicle, rail tank car or ISO tank, a suitably qualified engineer should be called to confirm the equipment is safe to continue to be used. If possible an engineer from the company providing the transport equipment should be called to verify this. In any event shipment should not recommence until the carrier or their appointed agent has agreed that it is safe to do so. For intermediate bulk containers (IBC) careful inspection should be made of discharge valves, pressure relief valves where fitted, lids, loading points and seams. If there is no visible damage to these components, and the pallet is still serviceable, the container can be used for the continuation of shipment. The seams and bungs of steel drums should be carefully examined. If there is no product seepage they can continue in transit if loaded vertically and secured.

4.3.2 ASSESSMENT –DAMAGED AND/OR LEAKING TANKS OR CONTAINERS

In these circumstances it is essential that precautions already outlined are strictly adhered to, notably:

- Taking instruction from the emergency authorities and incident “controller”.
- Ensuring the area is evacuated and nonessential personnel are up wind.
- The wearing of personal protective equipment specified for the product.

Containment

Any spillage should be contained as quickly as possible. Bunds to restrict the area may be made of sand, earth or other containment material. Shallow containers may be used to collect any product still being discharged.

Try to prevent the product from contaminating soil and water and entering any drainage systems and watercourses. diisocyanates will react with water (see Annex 1) and form insoluble polyureas thus blocking drainage systems. If material enters drainage systems it should be pumped out into open vessels at the earliest possible stage.

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

For bulk transport units, assessment of the location of leakage, its severity and effectiveness of any sealant method will determine whether, and how quickly, a replacement tank car will be required for the material to be transferred to it by pump.

For packed products, the leakage may be contained by sealing and/or placing the container in a position where the puncture is uppermost to prevent product loss. Replacement IBCs, new drums or oversized drums should be provided for leaking packages.

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

Neutralise the affected surfaces with liquid decontaminant and test the atmosphere for residual Diisocyanate vapour (see Annex 5 - sections 7-8). Re-establish the area as safe for the public or if in plant safe working conditions.

4.3.3 ASSESSMENT – RISK OF FIRE OR ON FIRE

Hazardous combustion products may include carbon monoxide, carbon dioxide, hydrogen cyanide, oxides of nitrogen and other toxic gases.

Full protective clothing and self-contained breathing apparatus has to be worn.

If the tank or container cannot be moved from the area in which the fire is located then a water screen (curtain) between the fire and tank/container should be used to minimise the heat effect on the tank or containers.

If a water screen cannot be safely enacted then direct water cooling of the or container's surface should take place to prevent distortion of the metal and possible thermal decomposition of the Diisocyanate.

Where the tank or container(s) is on fire then dry chemical powder, carbon dioxide or protein - based foam can be used as an extinguishing media. If water has to be used to extinguish the fire it should only be sprayed in large quantities.

Any damage to the tank or container will allow entry of moisture, particularly if water has been used. In this case a reaction will take place with the Diisocyanate to form solid polyureas.

The formation of solid polyureas may seal the rupture in the tank or container. The tank or drum or IBC may become pressurized by the buildup of solid material and gases. In order to prevent serious risk of rupture through pressure, the tank or container must not be resealed.

If it can be conducted safely then the tank or container should be vented to prevent build up of pressure. All precautions outlined for containment of spillage, and decontamination of the site, as outlined in Section 4.3.2, should be followed during the operation.

4.4. LEVEL 3 INTERVENTIONS - PROCEDURES FOR SPECIAL SITUATIONS

4.4.1. BULGING PACKAGES

A bulging package of diisocyanate is a result of contamination of the product, usually with water. The slow but continuous reaction with diisocyanate produces carbon dioxide and pressure increase. It is necessary to relieve this pressure safely before the packaging bursts. This is best accomplished by puncturing the top of it with a long spike or grapnel. During this action all uninvolved personnel must be evacuated and kept away from the area, and working personnel must have complete chemical protection. The punctured package must then be placed in a controlled area **until the end of the reaction**, before a definite solution is agreed with the supplier, as quickly as possible, for safe disposal. If transport is needed please make sure to put it in an oversize container fitted with a venting device. To make sure that no pressure build-up will occur venting in regular intervals is essential.

4.4.2. PACKAGES UNDER WATER

If an accident has led to containers falling into water, they should, if possible, be inspected for leaks. In the absence of leaks, the containers can simply be recovered, wiped dry and returned to the supplier. Depending on the situation, leaking packages can be sealed while still in the water or after being brought to land. In both cases the containers should be considered as potentially contaminated with the possibility of a pressure increase.

4.4.3. PACKAGES WHICH HAVE FALLEN OVER AND BURST OPEN

Large surface areas contaminated by liquid diisocyanate should be completely covered with dry sand or other mineral absorbers and the damaged packaging should be placed in an oversize drum. The personnel involved must wear protective clothing and breathing equipment.

The sand and any contaminated earth should be collected in open top drums for proper disposal. The drum lids must be capable of being vented in the case of any pressure increase. The site of the spill should then be thoroughly washed with a diisocyanate decontaminating liquid (see Annex 5 – section 7).

Following a precautionary determination for any residual diisocyanate in the air (see Annex 5), the location can be considered decontaminated.

If the evaporation of TDI has to be diminished immediately, cover the spillage with extinguishing foam.

4.4.4. CHEMICAL REACTION BETWEEN DIISOCYANATE AND POLYOLCOMPONENTS AS A RESULT OF DAMAGE TO A SPLIT COMPARTMENT TANKER OR THE INCORRECT FILLING OF TANKS

The combination of Polyol and diisocyanate components yields large amounts of heat and possible gas evolution. Once begun, this reaction is extremely difficult to stop. One goal must be to prevent bursting by means of controlled venting.

In storage, tanks releasing the combined material into the bund should be considered.

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

contamination and consequent reaction and heating up are moderate, try cooling down avoiding, if possible, direct contact with water.

All personnel involved must wear complete protective equipment.

Because of the potential, large amounts of heated diisocyanate vapors which can be involved, the evacuation of the immediate surroundings should be considered.

5. TRAINING OF EMERGENCY RESPONSE PERSONNEL

1. All ISOPA Members Companies undertake to ensure that these maintain a sufficient number of fully trained staff to deal with TDI and MDI transport emergencies. When preparing a training program for Emergency Response personnel, the following points should be considered:
 - a) the organisation, execution and evaluation of at least one full Emergency Response exercise per year : preferably a joint exercise with all ISOPA members
 - b) the analysis of all transportation incidents from own/other companies to learn from previous exercise
 - c) training/information on leak mending techniques
 - d) keeping in contact with other Emergency Response Teams to exchange knowledge and experience and report on incidents
 - e) information on existing National Transport Emergency Schemes to understand the approach in different national territories
 - f) practice in Emergency Response communication in English, to avoid communication difficulties at the scene of the incident; practice in reporting a transportation emergency
 - g) testing internal operative procedures aiming to provide most effective response and easiest co-ordination with National Transport Emergency Schemes and the requesting ISOPA Members Companies
 - h) basic knowledge of the legal aspects of dealing with a transport emergency
 - i) dealing with other parties at the scene of the incident - police, fire brigade, railway personnel, local authorities
 - j) knowledge of the product hazards on spills and leaks, also in combination with fire; first aid practices for diisocyanates, knowledge of the MSDS contents, definitions etc.
 - k) knowledge of the personal protection basics for MDI and TDI and binding agents in case of liquid spills
2. The Member Companies agree to share information (provided it is not sensitive under competition law) with other Members on all incidents and accidents in distribution in order to learn from best practice in dealing with incidents and accidents with TDI and MDI.

ANNEX 1

CHEMISTRY OF THE REACTION OF DIISOCYANATES WITH WATER

Reaction of diisocyanate and Water

When diisocyanate 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 (CO₂) and amines (R-NH₂).

The Amine (R-NH₂) 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 CO₂ gas.

Every 174 grams TDI consumes 18 grams water and produces 25 litre CO₂ 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 diisocyanate**

The hydrolysis of isocyanates 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 isocyanate 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**



ANNEX 2

PROPERTIES, HAZARDS AND SAFETY INFORMATION



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.

1.1 APPEARANCE



1.1.1 TDI

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

1.1.2 Polymeric MDI

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

1.1.3 Monomeric MDI

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

1.2 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 Harmonized 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.

1.2.1 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.

1.2.2 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.

1.3 MAIN PHYSICAL : CHEMICAL HAZARDS

TDI / MDI are NOT inherently explosive, nor are they oxidizers, 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 is** described in Annex 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 vapor 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 vapor 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.

1.4 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 vapor, aerosol and/or dust is the greatest concern by far.

Inhalation

Exposure to the vapor, 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 vapor, 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 isocyanates, but should wear glasses instead.

Skin contact

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

Swallowing

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

Long-term health effects

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

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

More safety information

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

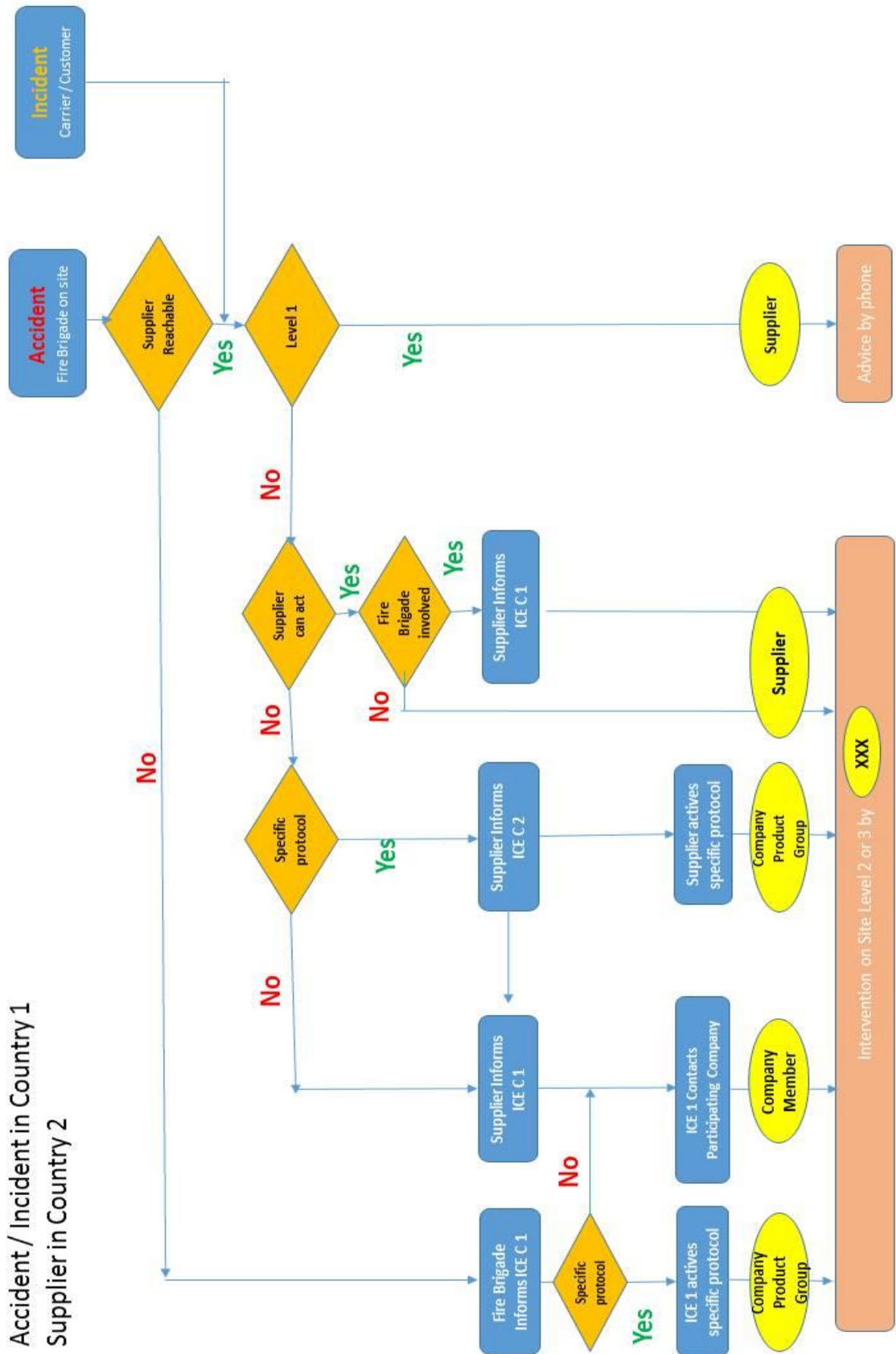
ANNEX 3

COMMERCIAL NAMES USED FOR MDI and TDI

<u>COMPANY</u>	<u>MDI /TDI</u>
BASF Polyurethanes GmbH	LUPRANATE M LUPRANATE T LUPRANAT VP ISOXXX/Y ISOXXX/Y BASONAT P
BORSODCHEM	ONGRONAT ONGRONAT
COVESTRO	DESMODUR DESMODUR – T
DOW	VORANATE ISONATE VORANATE - M VORANATE - T 80 ISONATE - M PAPI
HUNTSMAN	I-BOND SUPRASEC RUBINATE
SHELL	CARADATE

ANNEX 4

TECHNICAL HELP AND INFORMATION



ANNEX 5

RECOMMENDED EQUIPMENT FOR DEALING MDI or TDI TRANSPORT EMERGENIES

Individual companies should ensure that sufficient emergency equipment is readily available and that connection sizes, etc, are compatible with local operating conditions. The following list of equipment is recommended:

1 PERSONAL PROTECTIVE EQUIPMENT

- Overalls
- Goggles
- Impervious gauntlet gloves
- Full mask respirator with AB-filter
- Steel toed rubber safety boots
- Self-contained breathing apparatus
- Safety helmet

2 LEAK SEALING MATERIAL

- Wedges in different sizes and resistant material e.g. PTFE, wood, lead and braided lead, bandages made of neoprene rubber.
- Set of gaskets, cushions and bandages fitted with straps. Open shallow containers made of stainless steel or polypropylene (depth about 15-20cm) which are used to collect leaking material.

3 ABSORBANTS

- Mineral agent
- Sand
- Oilsorb
- Vermiculite

4 IF THE SPILLAGE CANNOT BE CONTROLLED,

TRANSFER TDI OR MDI BY PUMPING

Pump unit:

- membrane pump, explosion proofed, self priming
- peristaltic pump for pumping highly viscous fluids, explosion proof and self priming
- resistant hoses, metal hoses with all types of connections
- fittings for the most common European tanker connections

All equipment must be clean and ready for use.

5 STANDARD FITTINGS/COUPLINGS AND ADAPTERS

a) Tank cars

- Standard flange connection DN50
- English coupling Guillemain 3" to the German system TW (Tankwagen) MK50 (mm)
- Flange coupling DN 50 (mm) to TW MK80 (mm)
- TW VK 80 to TW MK 50
- MIL-C-27487 AMK3" to TW MK 50 (TW MK 50 is the female connection to the tank car)

b) Rail tank car

- 5 1/2" Withworth to TW MK 50

c) Eurotank

- Road container R3" to TW MK 50
- IBC container (content 1m³) S 59 x 4 1/2" to TW MK 50 (S means it cuts its own thread)

d) It is also useful to have a universal adapter or reducer of the type supplied by Elaflex. It is used in cases where a coupling does not fit or has been damaged or stuck. Order number KWK x MK 80.

e) A valve should be available which fits to TW MK50 for the purpose of closing the connection.

f) All sealings should be made of compatible material.

6 COMPLETE FIRE FIGHTING EQUIPMENT

Including dry powder and Foam extinguishers

7 DECONTAMINATING LIQUIDS

Formulation Weight or volume

Water 90 - 95%

Sodium carbonate 5 - 10%

Liquid detergent 0.2 - 2%

For routine operations e.g. decontamination of protective equipment tools and parts,

8 RECOMMENDED PROCESS FOR DECONTAMINATION

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-up ¹.
- 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 drum ².
- 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

9 AIR SAMPLING EQUIPMENT

a) Testing equipment with sampling tubes.

Producer Type

AUER or SA Gastester II 5146 – 701

Dräger GasspurpumpeGsG 21/31

b) Sampling tubes for TDI are available from Dräger.

c) Fast response monitor for the detection of a target gas. For example the MDA SPM Acutely Toxic Gas Monitor from Honeywell Analytics which is portable with a quick response time and range from 0-60 ppb. The monitor has a paper detection system and is suitable for both MDI and TDI. Another option could be the Isocyanate monitor from Scot Industries with the same options and a range from 0-200 ppb. For further details consult the internet.

10 SPECIAL EQUIPMENT FOR DEALING WITH DRUMS AND INTERMEDIATE

BULK CONTAINERS (IBCs)

- Oversized drums fitted with a top volve for venting
- Spike for puncturing bulging drums / containers

ANNEX 6

ISOPA EMERGENCY CALL INFORMATION SHEET

CEFIC / International Chemical Environment (ICE)

Date Time Name

Name of caller Company/Authority

Telephone Fax

Location of incident (road, town, country)

.....

What happened

.....

.....

Product name(s)

UN number Hazard number

Emergency Act Code Label

Product type: Liquid Pellets Solid Other

Incident type: Production Terminal Warehouse Road

Ship Rail Other

Containment: Tanker Drum IBC Container Bottle

Unit size/weight Total Amount damaged

Fire Spillage Amount of spillage Rate of leakage

Emergency Response Manual for Transport of TDI and MDI –

Remarks (weather, topography, environment)

.....

.....

.....

.....

Supplier

Carrier

Consignee

Measures taken by: Police Fire brigade Medic Driver

Other

.....

Type of help required:

LEVEL 1

INFORMATION

Product

Technical

Medical

LEVEL 2

EXPERT TO SITE

Product

Technical

Medical

LEVEL 3

EQUIPMENT TO SITE

Firefight

Technical

Clean-up

Action taken

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Spelling alphabet

A alpha	E echo	I india	M mike	Q quebec	U uniform	Y yankee
B bravo	F foxtrot	J juliet	N november	R romeo	V victor	Z zulu
C charly	G golf	K kilo	O oscar	S sierra	W whisky	
D delta	H hotel	L lima	P papa	T tango	X x-ray	

ANNEX 7

INCIDENT REPORT FORM (Emergency Response Group)

COMPANY

PRODUCT DESCRIPTION

DATE OF INCIDENT

Location of the incident

Country

Railway Sea Road Production Distribution (warehouse)

DESCRIPTION OF THE INCIDENT

Quantity shipped Quantity spilled

Shipping point Destination

Cause of incident, actions taken and impact on persons and environment :

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.....
.....

MEDIA INVOLVEMENT

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.....
.....

FOLLOW-UP INFORMATION

(long term effect on human health and environment, learning experience)

.....
.....

ANNEX 8

ICE SCHEME - NATIONAL EMERGENCY NUMBERS

See

<http://www.cefic.org/Industry-support/Transport--logistics/Transport-Emergency-Scheme-/Transport-Emergency-Scheme/>

ANNEX 9

MUTUAL AID SCHEME

ISOPA EMERGENCY RESPONSE CENTERS

COMPANY 24 HOUR FOCAL POINT TELEPHONE NUMBERS

BASF +49 180 2273112

BORSODCHEM +36 48 511515

COVESTRO +49 214 3099300

DOW +31 115 694982

HUNTSMAN +31 181 292131

SHELL +44 1235 239670

ISOPA AISBL

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