

MDI and TDI: Safety, Health and the Environment.

A Source Book and Practical Guide

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2 Handling MDI and TDI

Pride in safety

Safety is a critically important aspect of all activities involved in the handling of chemicals. The protection of the health of those who may possibly be exposed to MDI and TDI and the preservation of the environment can never be seen as optional. Safety does not, of course, simply 'happen'. Safe working practices can be achieved only by the active management of all relevant tasks. A safety system must start at the top of the organization. Managers should wish to ensure that there is careful and responsible management of all safety-related activities, that adequate material and human resources are provided, and that safety is seen to be a business priority. The design and implementation of a safety system that is practical, that uses resources effectively, and that is understood and actively implemented by the entire workforce should call upon a wide diversity of knowledge and skills in any enterprise. A considerable body of technical knowledge will need to be available, and effective ongoing communication with many individuals inside and outside the group will be necessary. The ownership of safety and environmental protection is the responsibility of the entire workforce and there needs to be a clear understanding by all staff of their particular responsibility in the overall safety system. A successful safety system will therefore rightly be a source of considerable pride and satisfaction throughout any organization since it involves staff at all levels and the results will be plainly visible to all. The principles outlined below are equally relevant to any size of organization.

Successful systems

Successful systems that meet internal and external needs in an ongoing manner share several characteristics (Figure 2.1):

- they are owned and managed;
- they are recorded and communicated;
- they are assessed regularly and are subject to corrective action and improvement.

Owned and managed

A system has no life of its own. It cannot simply appear when it is needed, and it cannot revise itself to take account of new understanding and experience,

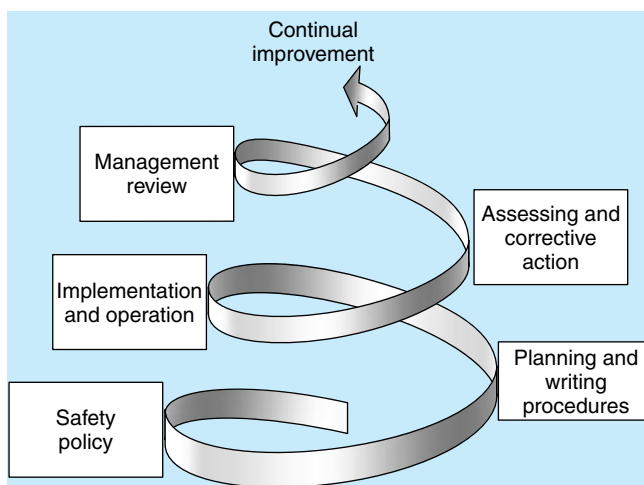


Figure 2.1 Characteristics of a successful safety system

or of changed circumstances. These matters must be the responsibility of an assigned manager of the safety system.

Recorded

All users of a system need to know how it works and what exactly they have to do. They must be involved in the compiling of the system, since safe working practices must take account of the practicalities of carrying out daily work. Clear and brief written procedures are a valuable source of communication and training material for new staff and will also be useful in refresher training. Written procedures will help to ensure they are not simply passed on verbally, possibly giving rise to poor work practices.

Assessed and improved

All systems can be improved, especially in the light of experience. Even the best systems can go wrong! The only way to ensure that everyone knows what is expected and that the agreed procedures are actually followed is by regular assessment or inspection. Any deficiencies in adhering to the system and any problems arising from the system itself will be the subject of corrective actions and, where necessary, of improved procedures. Improvement is thereby encouraged and is built into the system.

Safety systems for the handling of MDI and TDI

A safety system will need to pay attention to several key areas:

- *organizational matters*, including the clear allocation of responsibilities, requirements for measurement, reporting and communication, and mechanisms for review and improvement of the safety system;
- *operational procedures* for safe working, including those relevant to the handling of materials and to the operation and maintenance of equipment;

- *personnel matters* including training, and medical surveillance;
- *planning for emergencies*.

Each organization will develop its own list of critical safety procedures that are relevant to its own circumstances. All the general questions arising from ISO 9001, *Model for quality assurance in design, development, production, installation and servicing* are important and should be addressed in a comprehensive safety system. The further questions may need to be modified according to the particular polyurethane operation under consideration, and other questions will almost certainly arise in most operations.

General questions:

- Does the safety system cover all aspects of transportation, storage and use?
- Does everyone know what he or she is responsible for, and is this checked periodically?
- Are all critical procedures and instructions written down, and are current versions provided to those who have to implement them?
- Does the system meet all supplier, customer and regulatory requirements?
- Are all materials used in the production processes supported by adequate documentation, identification and stock control?
- Are there adequate inspection and test procedures to ensure safe working practices?
- Are substandard materials rigorously identified, labelled and segregated in such a way that they cannot be used accidentally?
- Are corrective actions put in place to correct deficiencies in the operation of the system, and to find solutions to any problems with the system itself?
- Are records available to demonstrate that all critical procedures are complied with, and is there a regular review of these records?
- Is adequate training and refresher training provided to ensure that all safety procedures are understood and can be properly implemented?

Further questions that may be relevant to the handling of diisocyanates:

- Is the latest safety information, especially that from suppliers, available on the diisocyanates and equipment that are being used?
- Is the MDI or TDI held at the correct temperature?
- Have adequate steps been taken to prevent contamination, especially by water?
- Are the safest methods used to transfer materials to the storage facilities?
- How is it known that safety equipment, including alarms, is available, is effective and is fully functional at all times?
- Does the system prevent unacceptable releases of diisocyanates to the workplace or the environment?
- Is the ventilation system able to cope with likely changes in conditions caused, for example, by fans, open doors and windows?
- Are changes in manufacturing processes accompanied by workplace monitoring (industrial hygiene sampling)?
- Is there regular diisocyanate medical surveillance for the potentially exposed workforce?
- Are adequate emergency procedures in place and tested?

Many organizations have decided to develop their safety systems further to the extent of having them submitted for regular internal audit, or for registration under national or international quality assurance standards with regular external audit. By these means, companies ensure that their safety and environmental protection systems are maintained to a high standard, thus providing evidence of their competence.

Two important International Standards for systems that are appropriate for safety and environmental protection are

- | | |
|-------------------|---|
| ISO 9001:1994 | <i>Model for quality assurance in design/development, production, installation and servicing. There are related national standards.</i> |
| ISO 14001:1996(E) | <i>Environmental management systems – specification with guidance for use.</i> |

Check lists, which cover many important aspects of safety, are available.

- Bulk storage facilities and equipment (SPI, 1996a, 1996b)
- Inspection of transport equipment (ISOPA, 1992)
- Unloading rail tank cars (SPI, 1996c, 1996d)
- Unloading tank trucks/ road tankers (SPI, 1996e, 1996f; ISOPA, 1992)

Diisocyanate suppliers and trade associations should be approached for further lists.

Information for the safety system

The working procedures that are part of the safety system will need to take account of the best practices elsewhere and of local conditions, so that effective solutions can be provided. It is clearly useless, for example, to write down procedures that are going to be disregarded because of the lack of equipment, because of lack of understanding, or because their implementation would interfere with other required work activities. This part of the book is concerned particularly with work practices that have been found to be satisfactory in very many companies, and which form the foundation for many safety procedures. Detailed work practices are examined that are relevant to safety in the transportation, storage and the handling of MDI and TDI in the workplace. Several Key Themes have been identified that are relevant to many operations, and which will provide useful information in the design of safety systems. These are:

- Key Theme 1: Know your product
- Key Theme 2: Protecting health
- Key Theme 3: Neutralization, decontamination and disposal of wastes
- Key Theme 4: Using personal protective equipment
- Key Theme 5: Monitoring exposure
- Key Theme 6: Dealing with accidents

Each Key Theme has been written to be used as an independent text and there is, therefore, some repetition of basic concepts and information.

Key Theme 1: Know your product

In this text, the term *Material safety data sheet* (MSDS) is used. In the European Union the term *Safety data sheet* may be used.

In order to handle chemicals safely, it is necessary to know their toxicological, chemical, physical and fire properties. This Key Theme provides the information on the basic properties which is needed for the safe handling of polymeric MDI, pure MDI and TDI. The properties of MDI or TDI as related to handling are almost the same, irrespective of supplier. However, there is a very wide diversity of other MDI- and TDI-based products, including chemically modified diisocyanates and solvent grades, and these have their own specific properties. In order to be able to handle these proprietary products safely it will be necessary to consult documentation from the supplier, notably the material safety data sheets. The headings often included in material safety data sheets are listed below, along with the relevant parts of this book in which there is detailed information on those topics, as related to polymeric MDI, pure MDI and TDI.

Topics covered by manufacturers' material safety data sheets

| Topic | Source |
|---|--|
| Hazards of the substance or preparation | Part 2, <i>Handling MDI and TDI: Key Theme 2, Protecting health</i> Part 3, <i>Health</i> Part 4, <i>The environment</i> Part 5.5, <i>Fire behaviour of MDI and TDI</i> |
| First aid measures | Part 2, <i>Handling MDI and TDI: Key Theme 6, Dealing with accidents</i> Part 3, <i>Health</i> |
| Fire-fighting measures | Part 2, <i>Handling MDI and TDI: Key Theme 6, Dealing with accidents</i> |
| Accidental release measures | Part 2, <i>Handling MDI and TDI: Key Theme 6, Dealing with accidents</i> Part 2, <i>Handling MDI and TDI: Key Theme 3, Neutralization, decontamination and disposal of wastes</i> |
| Handling and storage | Part 2, <i>Handling MDI and TDI: The workplace: storage and use of MDI and TDI</i> |
| Exposure controls and personal protection | Part 2, <i>Handling MDI and TDI: The workplace: storage and use of MDI and TDI</i> Part 2, <i>Handling MDI and TDI: Key Theme 4, Using personal protective equipment</i> |
| Physical and chemical properties | Part 5, <i>Supporting sciences: Parts 5.3 and 5.4</i> |
| Stability and reactivity | Part 5.3, <i>Chemical reactions of MDI and TDI</i> Part 4, <i>The environment</i> |

| | | |
|----------------------------------|-----------|---|
| Toxicology | Part 3, | Health |
| Ecotoxicology | Part 4, | The environment |
| Disposal | Part 2, | Handling MDI and TDI: Key Theme 3, Neutralization, decontamination and disposal of wastes |
| | Part 2, | Handling MDI and TDI: The workplace: storage and use of MDI and TDI |
| Transport | Part 2, | Handling MDI and TDI: Transport of MDI and TDI |
| Regulatory exposure requirements | Part 5.6, | Occupational exposure limits, stack limits and community limits |

Some useful properties of the commonly used MDI and TDI products are given in Table 2.1. More extensive data will be found in *Part 5.3, Chemical reactions of MDI and TDI* and *Part 5.4, Physical and fire properties*.

Table 2.1 Basic information on MDI and TDI.

| | Polymeric MDI | Pure MDI | 80/20 TDI |
|--|---|-------------|----------------------------------|
| Appearance | Brown liquid | White solid | Colourless to pale yellow liquid |
| Relative density at 20 °C (to that of water at 4 °C) | 1.24 | 1.33 | 1.22 |
| Melting point °C (°F) | 5 (41) | 40 (104) | 10 (50) |
| Viscosity at 20 °C cP (=mPa s) | Slightly viscous liquid 300 (product dependent) | Solid | Mobile liquid 3 |
| Reaction with water | Interact slowly with release of carbon dioxide gas | | |
| Fire properties | Not easily ignitable and not explosive | | |

At factory temperatures, both polymeric MDI and 80/20 TDI are liquids, whilst pure MDI is a solid. All are significantly denser than water (Table 2.1) and will therefore sink when in water or aqueous mixtures. Both polymeric MDI and TDI can solidify at low temperatures which may be encountered during transport and storage. The temperatures at which they are to be processed will often determine suitable storage temperatures for polymeric MDI and TDI. It is usually best to maintain them at 15 to 25 °C (59 to 77 °F): this gives a suitable balance of viscosity and product storage life. Pure MDI melts at about 40 °C (104 °F) and must be either stored frozen below 5 °C (41 °F), or held in the liquid state between 40 and 45 °C (104 and 113 °F). More information is given in *Part 2, The workplace: storage and use of MDI and TDI*.

MDI and TDI are reactive chemicals. The diisocyanates react with a range of common chemicals, in many cases vigorously with the evolution of heat. All contamination of MDI and TDI must be rigorously avoided. Contamination with water, including moisture from the air, will lead to the generation of

carbon dioxide. This will result in the development of excess pressure in closed containers. This pressure build-up can be sufficient to rupture a sealed drum with great violence. Alkalis such as sodium hydroxide or potassium hydroxide can react violently with diisocyanates.

Both MDI and TDI are very much less volatile than water. TDI has a saturated vapour concentration about one thousandth of that of water. At room temperature MDI is even less volatile, with a saturated vapour concentration of about one ten millionth of that of water. However, even very low concentrations of MDI or TDI can cause respiratory problems whether as vapour or as aerosols.

Usual state of MDI and TDI in air

| | |
|---------------------------------------|-----------------------|
| MDI | Vapour and/or aerosol |
| TDI | Vapour |
| Spray applications with MDI or TDI | Aerosol |

Health

Over-exposure to MDI or TDI can lead to adverse respiratory effects, which may include the development of asthma (Table 2.2). Strict observance of the permitted occupational exposure limits is therefore necessary. Once asthma has developed, and a person has become sensitized to a diisocyanate, even concentrations well below the permitted exposure levels can be sufficient to induce an asthmatic attack. Vapours, aerosols or splashes of MDI or TDI may cause irritation to the eyes. MDI and TDI are moderate skin irritants, and may cause skin sensitization or dermatitis in rare cases. Both MDI and TDI have low toxicities when swallowed. If any health problems occur that are thought to be associated with over-exposure to the diisocyanates, then medical attention should be sought immediately.

Table 2.2 Health effects of MDI and TDI.

| | Pure MDI | Polymeric MDI | 80/20 TDI |
|---------------------|---|---------------|-----------|
| Odour | Cannot be detected by smell unless concentrations are well above the occupational exposure limits | | |
| Respiratory effects | May cause respiratory irritation and asthma | | |
| Eye irritation | May be irritant to the eyes | | |
| Skin irritation | May cause moderate skin irritation | | |
| Oral toxicity | Have very low toxicities when swallowed | | |

Long-term studies on the health of workers exposed to MDI or TDI have shown no exposure-related clinical effects other than the development of respiratory symptoms. Animal studies, which give further background information, are discussed in *Part 3, Health* of this book.

See Part 5.6, *Occupational exposure limits, stack limits and community limits* for more detailed information.

Occupational exposure limits are indicators of airborne concentrations of substances to which nearly all workers may be repeatedly exposed day after day without adverse health effects. They are usually mandatory for many chemicals. There is good agreement globally on the limits that should apply to short-term exposure (for example, 15 min) or long-term (8 h) exposure. The limits for airborne MDI or TDI may be expressed in parts per billion (volume in volume of air) or in concentration (weight in volume of air). Table 2.3 gives the limit values commonly adopted for airborne diisocyanates.

Table 2.3 Occupational exposure limits: typical values.

| | Short-term (15 min) | | Long-term (8 h) | |
|-----|---------------------|-----|-------------------|-----|
| | mg/m ³ | ppb | mg/m ³ | ppb |
| MDI | 0.2 | 20 | 0.05 | 5 |
| TDI | 0.14 | 20 | 0.036 | 5 |

It can be seen that the limits for MDI and TDI are the same when they are expressed in parts per billion, and very similar when expressed as milligrams per cubic metre. At 20 °C (68 °F) MDI will not volatilize enough to achieve the short-term occupational exposure limit, whereas TDI will significantly exceed the limit, as shown in Figure 2.2. At 30 °C (86 °F) saturated vapour concentrations of MDI and TDI both exceed the occupational exposure limits.

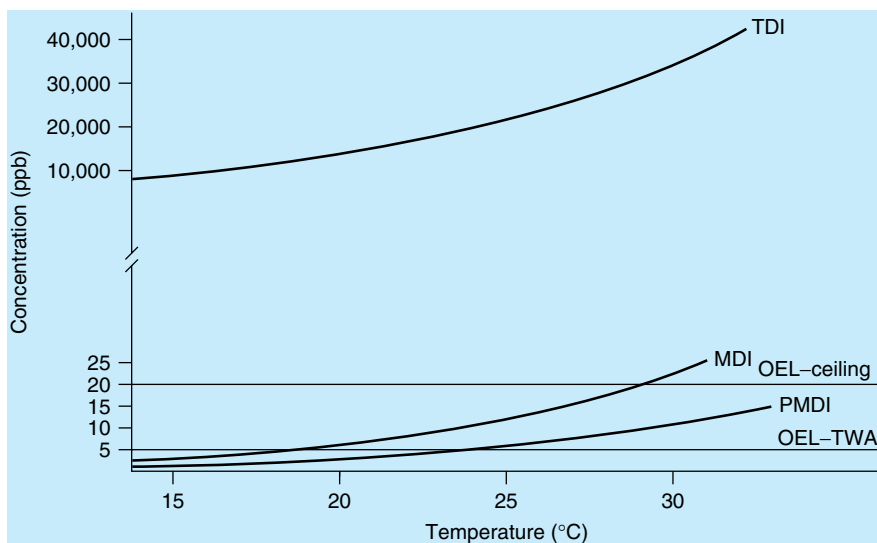


Figure 2.2 Vapour pressure-temperature curves for MDI and TDI

Environment

See Part 4, *The environment*.

Releases of MDI or TDI into the environment are not persistent, being degraded in air and in water. The diisocyanates are so inherently reactive in water as to be

virtually unavailable for biological uptake or bioaccumulation, and the major products are inert, insoluble polyureas. As a result, environmental exposure to MDI or TDI, arising either from normal use or accidental release, is very low. Both MDI and TDI show generally low toxicity to a wide range of water- and soil-based organisms: bacteria, algae, fish, invertebrates and plants.

Key Theme 2: Protecting health

First aid guidelines are given in Part 3, Health.

Duty of care

All possible routes of exposure should be avoided. Avoidance of inhalation of MDI or TDI as vapour, aerosols or dusts is of particular importance because of possible respiratory problems.

The transport, storage and use of MDI and TDI should not therefore be undertaken without a proper understanding of the potential health risks involved. There need to be effective systems for the protection of the health of personnel in the workplace. At all times the guiding principle must be to ensure that releases of all types are below those levels at which adverse effects may occur. Good workplace procedures are essential. Engineering design of polyurethane manufacturing equipment and controls should be used whenever possible to reduce exposure to diisocyanates. Adequate ventilation is usually necessary to prevent worker exposure for many processing operations involving MDI or TDI. Planning must nevertheless also take into account how to respond to those situations where excessive short-term releases occur because of an accident. The implications of normal or accidental releases on the nearby community also need to be considered. Experience over the past 30 to 40 years has shown that the application of these principles of minimizing human exposure has led to a continuous reduction in adverse health effects. Companies should be encouraged to develop their safety-at-work systems as an on-going activity.

The occupational exposure limits in force must always be observed. The procedures necessary will normally include a programme of workplace monitoring and documentation to ensure compliance. It is necessary to measure the concentrations of diisocyanates in the atmosphere to find out if any situations require corrective action. Some direct reading analytical instruments are available for this purpose (see *Part 5.7, Sampling and analysis*). It is imperative that built-in safeguards such as alarms are used to alert workers to over-exposures. There should be good evidence to show that these safeguards are fully effective at all times.

Over-exposure to MDI or TDI may cause irritation of the nose and lungs, feelings of tightness in the chest and difficulty in breathing; repeated over-exposure may lead to asthma-like attacks. MDI and TDI may also cause irritation of the eyes and skin.

Training in first aid specific to the handling of MDI and TDI should be provided for staff in all workplaces where diisocyanates are handled. It should

be standard practice to ensure that all staff working in areas where diisocyanates are transported, stored or used have a full understanding of the potential health effects and of the safe working practices recommended for their site. These should include first aid and decontamination procedures to be followed in the event of a spill or leak. First aid treatment is discussed in detail in *Part 3, Health*.

Exposure: how can MDI or TDI enter the body?

It is obvious that there can be no health impact if substances are prevented from entering the body in the first place. The entry points for chemicals into the body are:

- into the respiratory system (Figure 2.3) by the inhalation of a vapour, aerosol or dust;
- through the skin, especially if damaged by cuts or open wounds;
- by contact with the eye;
- through the mouth by swallowing, or by eating contaminated food or drink;
- by smoking.

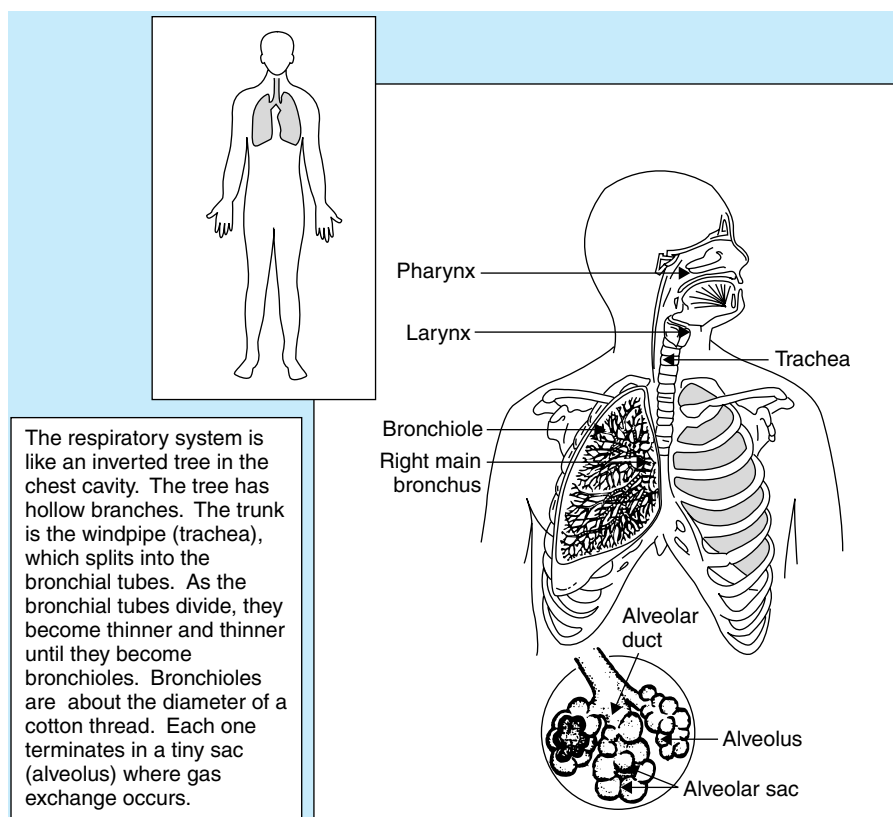


Figure 2.3 The human respiratory system

MDI and TDI react readily with biological substances, and will thus not circulate around the body in their original forms.

Possible types of exposure

As vapour

If workplace air containing MDI or TDI is inhaled, some of the diisocyanate can be carried into the lungs after passing the throat and upper respiratory tract. At ambient temperature, the vapour concentration of TDI may exceed the long-term occupational exposure limit. The vapour concentration of MDI can reach the occupational exposure limit at elevated temperatures. At the extremely low concentrations usually found in the workplace, MDI and TDI as vapours are carried along with the air with which they mix. There is no separation or layering.

As aerosol

In certain situations very small droplets or particles (aerosols), of MDI in particular, may be produced. In contrast to gases, which contain individual molecules of diisocyanate, aerosols are particles of liquid or of solid, containing many molecules. Whilst it is sometimes possible to see mists of larger droplets, many aerosols are quite invisible to the naked eye even under favourable lighting conditions. These smaller particles are of special concern because they have the potential to be inhaled and carried into the lungs. Only those particles of less than about 10 to 15 μm are respirable; larger particles are deposited in nasal passages and the upper respiratory tract. Larger aerosol particles may be deposited on working surfaces, where they could give rise to skin contamination. Spraying operations are the main source of aerosols. Aerosols are also produced when a vapour at elevated temperatures cools to below its saturated vapour concentration. Aerosols of reacting mixtures of polyurethane components may be present in spraying operations. In these cases the concentration of diisocyanate decreases rapidly as the reaction proceeds.

See *Part 3, Health* for more details on exposure to aerosols.

As dusts

Dusts of pure MDI may be encountered when flaked, solid material is handled, or if solid residues are cleaned up by scraping or brushing. It is also possible for particles of dust from other workplace materials such as wood to have diisocyanates adsorbed in certain circumstances. Particles of less than about 10 to 15 μm are respirable.

As liquids

Exposure may occur by contact of the skin or the eyes with polymeric MDI or TDI or with any form of MDI or TDI dissolved in solvents.

Medical symptoms

See *Part 3, Health* for detailed information.

There are usually no health effects resulting from exposure to MDI or TDI below the occupational exposure limits. However, a brief, single high exposure to diisocyanates may trigger an airway response, even if the average concentration for a period of 15 min is below the permitted occupational exposure limits. The topic is covered in more detail in *Part 3, Health* and occupational exposure limits are discussed in *Part 5.6, Occupational exposure limits, stack*

limits and community limits. The onset of the clinical signs of irritation, such as watering eyes, sore throat, or cough, occurs at much higher levels than the permitted occupational exposure limits.

At the maximum allowable workplace exposure levels MDI and TDI cannot be detected by the human sense of smell. Odour should never be relied upon as an indication of exposure to MDI or TDI. If a worker can smell them, over-exposure is occurring.

Odour thresholds

Odour thresholds for TDI and MDI have been determined by exposing panels of volunteers to different levels of the test substance. In one study (MCA, 1968) recognition of the odour of TDI was achieved by 50 % of the panel at 200 ppb TDI, but over 2000 ppb was needed for 100 % recognition. In another study (Henschler *et al.*, 1962), 50 ppb was sufficient for over 90 % recognition. The odour of polymeric MDI was detectable at 400 ppb according to one report (Woolrich, 1982). Too much emphasis should not be placed on these values as:

- the values may not be accurate due to some of the analytical and sampling methods used.
- obtaining stable concentrations of diisocyanate vapours and aerosols in a test room is very difficult due to their adsorption onto surfaces.
- human odour perception is very unreliable and fatigues easily at threshold levels.

From inhalation

The main risk from diisocyanates arises from inha-lation of vapours, aerosols or dusts. MDI and TDI will act primarily as respiratory irritants. In *mild* cases the affected person may experience slight irritation of the nose and throat, possibly combined with dryness of the throat. In *severe* cases the person may suffer acute bronchial irritation and difficulty in breathing. Individuals who have developed sensitivity to MDI or TDI may develop asthma and experience wheezing, tightness of the chest and shortness of breath. Symptoms of both

irritation and sensitization may be delayed for several hours after exposure. Coughing at night may be a symptom of sensitization. A hyperreactive response to even minimal concentrations of MDI or TDI may develop in sensitized persons or in persons with hyperreactive airways.

From skin contact

MDI and TDI are moderate skin irritants. In rare cases, repeated or prolonged contact may cause skin sensitization. There are differing views of researchers on the possible contribution of skin contact of MDI and TDI to the development of respiratory disease.

From eye contact

TDI in the form of an aerosol, liquid or vapour may cause eye irritation. In very rare instances, severe eye contamination may cause lasting damage (corneal scars). Overall, MDI appears to be somewhat less irritating.

Medical checks

Minimization of exposure is the prime defence against health problems and should be supported by engineering controls, by regular monitoring of workplace exposure where appropriate, by the use of relevant protective clothing and by proper education of the work force. These measures should be supported by active medical surveillance of the workforce. Various systems are in

operation in different countries, in part to meet particular national requirements such as those for compensation schemes. National requirements must always be followed in setting up a medical surveillance scheme for diisocyanate workers. Medical surveillance concentrates on the respiratory tract, in which most problems occur in practice. This surveillance usually involves measuring lung function and compiling a detailed respiratory history.

The most commonly used way of determining lung function in humans involves measuring the rate and extent to which the lungs can move air in and out of the respiratory system by constructing a flow–time curve depicting air movement over time (Figure 2.4). Testing is typically conducted under conditions requiring maximal effort by the person being evaluated. Flow-volume data may be produced in graphical or digital format depending on the type of measuring device (spirometer) selected. Standard prediction equations or reference tables have been developed for different groups of people to improve the clinical interpretation of spirometric results, because the ventilatory capacity of the lungs is known to decline gradually with increasing age, even in the healthiest of individuals. Data from flow-volume measurements may depend on many other variables, including stature, gender, race, nutritional state, health, smoking history, weight and physical fitness. The interpretation of lung function data is a specialised task.

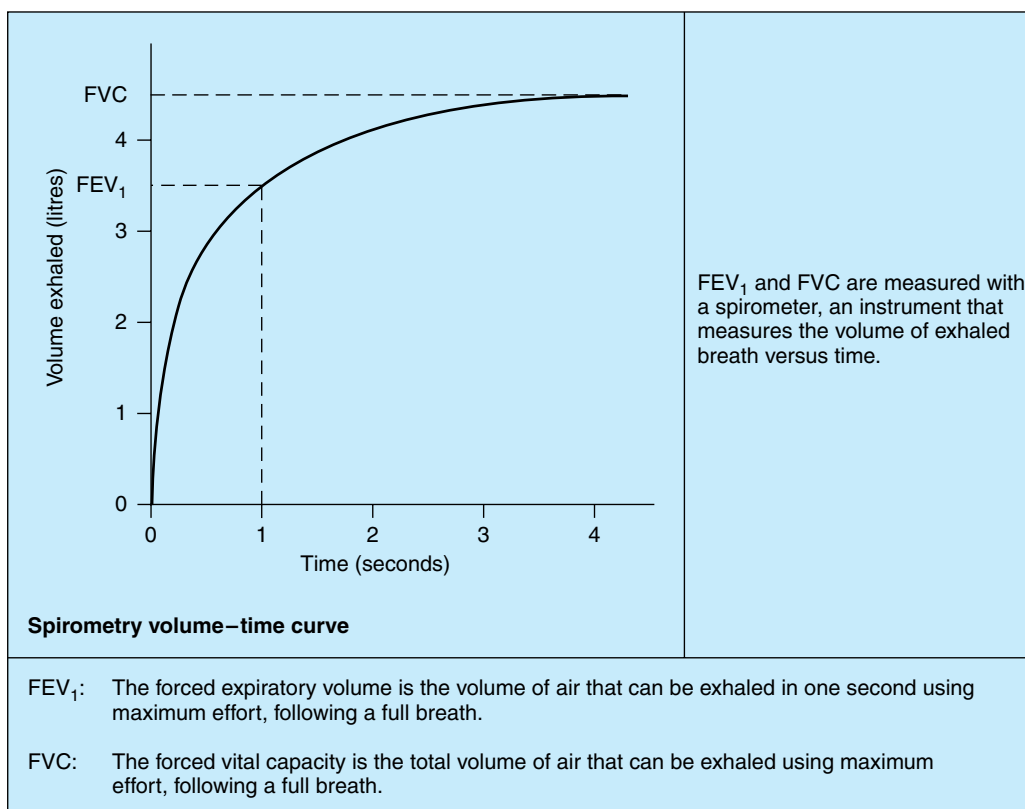


Figure 2.4 Spirometry

It is normal good industry practice for lung functions to be measured:

- prior to employment in work with MDI or TDI;
- during routine monitoring of health;
- on return to work after certain illnesses;
- if respiratory problems are suspected by medical staff;
- as part of the diagnosis of asthma;
- as part of a final examination on leaving employment using diisocyanates;
- after incidents or emergencies involving diisocyanates.

The most common parameters derived from the volume–time curves are the forced expiratory volume in one second (FEV₁) and the forced vital capacity (FVC). Accurate measurement of these parameters requires the active cooperation and maximum effort of the individual being tested. Standards have been developed to assure the consistency and accuracy of results. For example, at least three tests are generally performed so that reproducibility may be judged. In part because of their simplicity, FEV₁ and FVC have remained the most widely used measures for describing lung function performance.

Regulatory bodies and other organizations may issue recommendations for medical surveillance of diisocyanate workers. Such recommendations may include:

- a pre-placement examination;
- routine periodic examinations;
- re-examination on return to work following a sickness absence.

Health surveillance recommendations
HVBG (1998); HSE (1997a, 1998); BRMA and Rapra (2001); NZ OSH (1998).

Timing of examinations

- *Pre-employment:* a pre-placement examination will provide a baseline for each employee against which any subsequent examination can be compared to detect changes, and to identify subjects at increased risk due to existing respiratory disease. Testing will also check whether workers have the ability to use respirators, if needed. A pre-employment examination is obviously not possible where a health-surveillance scheme is introduced into an existing workforce, and an initial examination at the time of introduction must be performed as a baseline.
- *During employment:* examinations at 2 and 6 weeks after the start of diisocyanate work are also recommended in workplaces with measurable levels of diisocyanates, to identify those people who may become sensitized rapidly, or who react adversely even to very low atmospheric diisocyanate concentrations because of pre-existing nonspecific bronchial hyperresponsiveness. Thereafter, it is of value to carry out routine examinations at intervals. The interval may range from 3 months to 2 years, depending on the prior medical history and the expected exposure levels of an individual.
- *After absence for sickness:* if a diisocyanate worker has had significant absence due to respiratory disease, the examination should be repeated. Significant sickness absence is considered to be more than 2 weeks, or repeated shorter absences.

- *Final examination*: it is desirable to have a final examination at the time of finishing diisocyanate work. This is useful in order to assess whether any subsequent illness is related to diisocyanate exposure.

Content of examinations

The following is recommended as a minimum:

- *History*: interview with a structured questionnaire. An example of a suitable questionnaire is provided in *Part 3, Health*. This should cover the general medical and occupational history with special attention being paid to chronic and allergic chest diseases, and to smoking.
- *Clinical examination* with emphasis on the respiratory system.
- *Pulmonary function tests*: normally forced expiratory volume in one second and forced vital capacity.

Spirometry: further considerations

A correctly calibrated spirometer operated by trained staff is essential. Ideally, examinations during employment should take place at the same time of day to allow for diurnal variation and should correspond as closely as possible to the times of diisocyanate exposure. A fall of greater than 0.25 l on the mean corrected FEV₁, measured on two separate occasions after allowing for the ageing effect, is considered significant. It may also be useful to measure flow rate versus lung volume (a flow–volume loop), which can help in identifying abnormal lung functions.

Conduct of medical examinations

Any scheme must take account of local regulatory requirements. The examinations are best conducted by a physician with training and experience in occupational medicine. Whilst the measurement of peak flows at intervals throughout the working day is useful in diagnosing occupationally-related bronchoconstrictive problems

(see *Part 3, Health: Diagnosis of diisocyanate asthma*), it is not of particular value in the routine screening of an asymptomatic individual. Records of medical surveillance should be retained. For example, a retention period of 40 years is required under the relevant regulations in the UK (HSE, 1998).

The pre-placement examination may identify subjects suffering from hay fever, recurrent acute bronchitis, pulmonary tuberculosis, asthma, chronic bronchitis or interstitial pulmonary fibrosis, whatever their cause, occupational or otherwise. The physician may decide that, because of the pre-existing disease, an individual could be at particular risk from additional exposure to chemicals in the expected work environment. In this situation the physician may decide that the potential additional risks should be fully explained so that the subject can make an informed decision about the type of employment most suitable in his or her own circumstances.

If, on routine surveillance examination, signs and symptoms of asthma are noted (see *Part 3, Health*), the physician should investigate the causes without delay. It may be recommended that the individual be relocated to another job where there is no possibility of further diisocyanate exposure.

Key Theme 3: Neutralization, decontamination and disposal of wastes

In this text, *neutralization* means treating MDI or TDI with a solid or liquid neutralizer to destroy the isocyanate groups and hence minimize exposure

of humans or the environment. *Decontamination* means removing all traces of these diisocyanates from the given surface or area. These topics are discussed in the contexts of the routine cleaning of machinery and drums and of accidental spillage. It is important to understand the key principles of neutralization and decontamination, otherwise new problems may be created during the cleaning process.

There are potential problems associated with the process of neutralization. The liberation of carbon dioxide and heat can lead to drum rupture if the drums used for neutralization are sealed before the neutralization reaction is fully completed. Ammonia-based neutralizers can lead to over-exposure to ammonia. Use of a neutralization formula containing a strong alkali may accelerate the formation of diamines from diisocyanates, and this needs to be taken into account when disposal of neutralization residues is considered.

Types of neutralizer

Absorbent material/solid neutralizers

- *Wet sand.*
- *Wet earth.*
- Other inorganic materials such as kieselguhr, 'kitty litter' (which is granulated clay) or proprietary absorbents. Fuller's earth is sometimes recommended, but has the disadvantage that it will turn to a mud-like consistency when mixed with water.
- *Wet sawdust* is useful for dealing with minor spills on floors. Dry sawdust may sometimes be a fire risk, particularly in large quantities.

Liquid neutralizers

Neutral

- Water and surfactant (surface active agent): the use of surfactant allows better dispersion of water with MDI and TDI, which are immiscible with water.

Alkaline

- Water, surfactant and sodium carbonate: this mixture reacts faster than water and surfactant alone.
- Water, surfactant and ammonia: this reacts faster than a mixture consisting of water, surfactant and sodium carbonate.
- Water, and an alcohol (for example, isopropanol) and ammonia.

Routine cleaning of equipment and drums

Cleaning of equipment

Any diisocyanate in the equipment will need to be neutralized; polyurethane or polyurea deposits may also need to be removed. Polyurethane deposits may build up in some equipment, for example in mixing heads. Polyureas may be formed in equipment that has been dismantled for subsequent cleaning if left open to atmospheric moisture. One neutralizer that may be used contains

Caution

Concentrated aqueous ammonia is subject to an occupational exposure limit, and precautions should be taken to avoid inhaling the toxic vapours. This neutralizer may also cause a very fast neutralization reaction, so do not use it in closed containers or confined spaces.

industrial alcohol: this should be adequate for parts that are contaminated only with the unreacted diisocyanates. More vigorous decontamination procedures may be needed in some situations and it may be necessary to use highly polar organic solvents such as dimethylsulphoxide (DMSO), dimethylformamide (DMF), or *N*-methylpyrrolidone (NMP). In the case of very bad contamination, molten salt baths or even surface blasting of components may be useful. The blasting agent should be chosen so as not to damage engineered surfaces. For all these cleaning processes, there should be no exposure of humans to the systems. The suppliers of chemicals and equipment should be consulted to ensure that recommendations for safe cleaning practices are obtained. Disposal of solvents containing diisocyanates, whether from routine solvent flushing of mixing heads or from separate cleaning of machine parts, should be in accordance with instructions from the suppliers and with local or regulatory requirements.

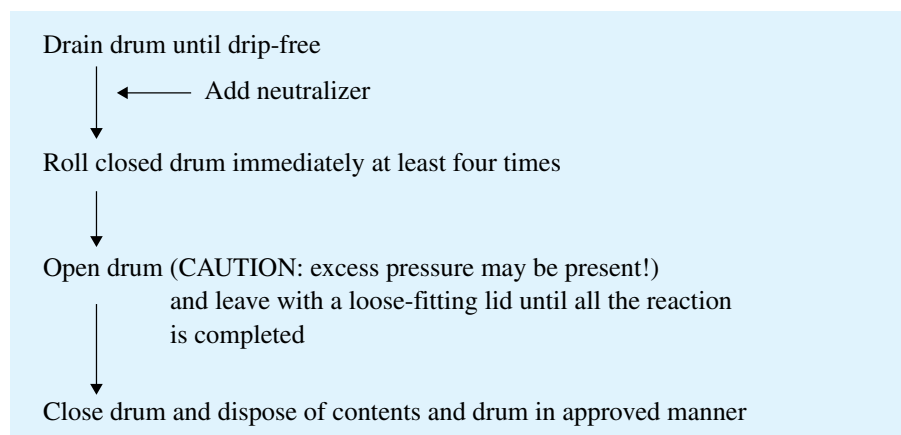
Drum cleaning

Here it is necessary to consider the disposal both of drums which are drip-free and of drums which contain considerable quantities of unusable products such as material used for cleaning machine lines. There are significant differences in the handling of these, according to regulations and the availability of local specialist facilities. These topics are discussed in greater detail in *Part 2, The workplace: storage and use of MDI and TDI*.

Drum decontamination and disposal

When drums have been pumped out or drained to leave as little residue as possible, there are two possible approaches (see *Part 2, The workplace: storage and use of MDI and TDI* for further details):

- Seal the drum immediately and send to a drum-handling specialist.
- Decontaminate the drum using a slow reacting water-based neutralizer. On no account should fast reacting systems be used or catalyst added. The drum should be partially filled with neutralizer Formulation 1 or 5. One to one and a half litres (approximately a quarter to a half a US gallon) should be sufficient (ISOPA, 1997a). The following sequence can be used.



Polymeric MDI and TDI can be neutralized at about 25 °C. Higher viscosity materials, such as some modified MDIs and TDIs, may need to be warmed to give low enough viscosities to allow mixing with the neutralizer.

Disposal of large quantities of diisocyanate

The disposal of large quantities of MDI or TDI should normally be undertaken only by a specialist contractor. If, however, it is necessary to dispose of up to a drum full of diisocyanate this should be undertaken with extreme caution, and expert advice should be sought.

There are two problems that may arise in neutralizing diisocyanates in bulk:

- Contaminants in the diisocyanate may cause a very rapid reaction to take place, with the liberation of carbon dioxide gas.
- Incomplete neutralization may occur because of inadequate mixing of the neutralizer and the diisocyanate. The diisocyanate is about 25 % denser than water so that even if there has been drum rolling to mix the diisocyanate and water, two layers will form once the drum is stationary. In that situation a barrier of solid polyureas will form, separating the two layers. This may then lead to large quantities of diisocyanate not being neutralized even though there was an adequate quantity of neutralizer in the drum.

Rapid reaction may occur during the decontamination process, Elastogran (1997).

Any attempt at neutralization of large quantities of diisocyanate, even if the material is divided into smaller portions, could be construed by some regulators as *waste treatment operations*, which require a government licence.

It is important that large quantities of unusable MDI or TDI are not neutralized in a drum by adding liquid neutralizer to the diisocyanate. Diisocyanate should be added to the neutralizer with stirring, and not vice versa. The scale of such reactions should be reduced by dividing the contents into several small quantities before neutralization, if no other way of disposal is possible.

Disposal of diisocyanates as 'polyurethanes'

It was common practice to neutralize diisocyanates by adding waste diisocyanates to excess polyol (or polyol blend) to form polyurethane polymer, which was then disposed of (as landfill, for example). **This approach is not recommended** for two reasons. Firstly, since the approach leads to over-neutralization of the diisocyanate there will be an excess of polyol or polyol blend, which may cause pollution problems. Secondly, if polyol blend (including catalyst) is used, there may be a violent reaction during the neutralization process.

There is one situation in which polyurethane formation may be used effectively to neutralize excess diisocyanate. It is not unusual for excess diisocyanate to arise from metering trials. Typically both polyol blend and diisocyanate are metered together in the required ratio for complete reaction. Under such circumstances it is reasonable to mix the two (polyol blend and diisocyanate) metering shots together to form polyurethane. However, this should be done on a scale that excludes the possibility of violent reaction.

It should be emphasized that any polyurethanes produced in the neutralization processes above may be very crude, because the critical mixing conditions which are normal to polyurethane production are not observed.

Labelling of decontaminated drums

Labelling of containers is always important. Original labels should be kept intact. Once a drum has been decontaminated, a further label should be added. An example is given below. National, regional or local regulations will determine the labelling of such drums. MDI and TDI may require different labels.

| | |
|---|------------|
| This drum has been decontaminated using. . . | |
| The product contained in this drum should not be allowed to come into contact with soil or the aquatic environment. | |
| <i>Name of the decontaminating company</i> | |
| date: | signature: |

Disposal of decontamination residues

Wastes from decontamination procedures should be sent to specialist disposal companies, who will use incineration or landfill according to national, regional or local requirements. The representatives of MDI and TDI suppliers may be able to give contact addresses. There should be discussions with contractors to be sure that they are licensed according to local and national regulations and that they use lawful and safe means of disposal.

Neutralization after a spillage

Spillages may be contained by bunding (diking) in areas where losses may be foreseen: such areas include pump or tank areas, where maintenance work is common. Where spillages are in other areas they can be isolated by temporary barriers such as spill pillows or other devices. Materials which can be used for containment are wet sand, wet soil or wet sawdust. These can be used not only to contain the spillage but at the same time to adsorb and partially neutralize the diisocyanate because it reacts with water in these materials. *Key Theme 6: Dealing with accidents* gives further details of what to do in the event of spillage.

Floors

The main considerations here are that large volumes of spilled MDI or TDI may need to be handled, and that there may be significant contamination of porous or cracked floors before neutralizer is applied. A floor would normally serve as a heat sink, so a fast-reacting neutralizer may be used. However, ammonia-based neutralizers should be used only if ventilation is very efficient and/or emergency staff have air-supplied breathing apparatus.

Dealing with contaminated floors

- Absorb and neutralize diisocyanates on the floor using wet sand, wet earth, wet sawdust or proprietary absorbent. Add liquid neutralizer (Formulation 1, 2 or 3, below).
- Clean up the area. See *Disposal of decontamination residues* above.
- Add further liquid neutralizer and solid absorbent to the floor until air monitoring shows that no diisocyanate remains in the floor material.
- Avoid using ammonia-based neutralizer unless there is good ventilation.

A heavy-duty brush may be used to sweep the absorbent into the spill. After use, the brush should be placed in a plastic bag and then be disposed of properly, for example by incineration. An operator wearing suitable protective equipment should transfer the residues containing the diisocyanate to an open drum. Liquid neutralizer mixture should be added to the solid residues in the drum even if the solid was previously wetted with neutralizer. Sufficient should be used to give a considerable excess of neutralizer solution over the amount of diisocyanate estimated to be in the spill. This mixture of solid and liquid should be stirred occasionally, monitored for temperature build-up, and should stand for 1–2 days in a well ventilated place or outdoors to ensure that the diisocyanate has fully reacted. The container can then be sealed. A waste contractor should dispose of the residues by incineration or by landfill according to regulations or local practices.

Soil, water or roadway

This section refers to spillages outdoors, as associated with transportation accidents or storage tank failures. The key consideration is the protection of personnel, after which the diisocyanate should be contained to prevent run-off to drains or inaccessible areas. Although the environmental impact of MDI or TDI on air, soil or water is rather low, exposure should be minimized. Diisocyanates in water or soil are neutralized by the water and soil components, essentially to form polyureas which are biologically and chemically inert. However, the diisocyanate should be cleaned up in a rigorous way.

Soil

Where material has been spilled onto soil and absorbed, it will slowly become neutralized with the formation of solid polyureas. The contaminated soil may need to be removed to an area for neutralization and testing before being sent to landfill or incineration depending on regulations or local practices.

Water

Diisocyanates are immiscible with, and significantly denser than, water and thus will drop to the bottom of a pool or river. However, in highly turbulent conditions there may be some local distribution of globules of material. The diisocyanate will react once it is in contact with water. The rate of reaction

depends upon the specific diisocyanate, the water temperature and the degree of subdivision of the mass of diisocyanate. Usually, the reaction is rather slow, taking days or even weeks, especially as some diisocyanate may be trapped within the solid waxy mass which forms from the diisocyanate on reaction with water. Most of the reacted material, which is predominantly agglomerates of polyureas, remains submerged in water. However, sometimes these masses of polyureas may rise to the surface of the water due to trapping of carbon dioxide liberated in the reaction. Reacted material can be removed from the water by skimming the surface and dredging the bottom.

Roadway

Where MDI or TDI is spilled onto a road or similar surface, it will need to be isolated by surrounding with absorbent material. The diisocyanate can be neutralized by a covering of wet soil or sand, to which may be added alkali decontaminant (Formulation 2). Ammonia-based formulations should be used only if nonessential personnel have been excluded and/or there is significant air movement to disperse the ammonia gas. It is extremely likely that the diisocyanate will have penetrated the surface of the road. A further application or series of applications of neutralizer will be necessary until monitoring indicates that there is complete decontamination of the surface.

It is possible that spillages of pure MDI or of TDI may solidify on contacting a cold road surface. In such cases it will be necessary to remove this solid material from the road and then to mix it with absorbent/neutralizer mechanically. The road surface may need to be sandblasted to remove all the diisocyanate. In this case, the contaminated sand must be collected for subsequent neutralization and disposal. Respiratory protection is necessary.

Clothing

Contaminated clothing should be removed immediately and put into an impermeable bag. If there is any doubt about the presence of free residual diisocyanate the clothing must be decontaminated by soaking in neutralizer solution overnight. Depending upon the degree of spillage and any subsequent stiffening of the fabric, clothing may be disposed of or laundered by an industrial contractor.

Minor splashes on overalls/coveralls and other clothes are likely to be neutralized by moisture in the fabrics and may be laundered normally.

Treatment of contaminated clothing

- Soak clothing in liquid neutralizer (Formulation 1, 2 or 3).
- Leave overnight if contamination is excessive.
- Launder normally, wash separately from other clothing.
- Do not use ammonia-based solutions (Formulation 3), unless in a ventilated area.

It is an advantage to wear front-fastening overalls and shirts, so that diisocyanate spillages are not drawn across the face when the garments are removed.

Snap fasteners, instead of buttons, are ideal for rapid removal of overalls. Contaminated clothing may affect support personnel such as first aiders and physicians, unless precautions are taken.

Contaminated personal protective equipment

After contamination, protective equipment such as safety glasses, respirator face pieces and other reusable safety equipment should be decontaminated. Equipment may be cleaned by wiping it with absorbent cloths soaked in neutralizer, which themselves must be decontaminated by immersing in a neutralizer solution before disposal. Badly contaminated equipment can be immersed in neutralizer solution prior to disposal.

Neutralizer formulations

Liquid formulation without alkalis

Formulation 1

| | |
|------------|---------------------|
| surfactant | 1 % to 20 % |
| water | to make up to 100 % |

There is no comprehensive work that is able to define a 'best formulation' of surfactant and water. However, some preliminary work with TDI (Kiestler, 1999) suggested that higher concentrations of surfactant lead to a faster overall disappearance of TDI, and that ethoxylated surfactants were superior to anionic surfactants.

Liquid formulations containing alkalis

Formulation 2

| | |
|-------------------|---------------------|
| liquid surfactant | 0.2 % to 2 % |
| sodium carbonate | 5 % to 10 % |
| water | to make up to 100 % |

Formulation 3

| | |
|----------------------|---------------------|
| liquid surfactant | 0.2 % to 2 % |
| concentrated ammonia | 3 % to 8 % |
| water | to make up to 100 % |

Formulation 4

| | |
|--------------------------|---------------------|
| ethanol or other alcohol | 50 % |
| concentrated ammonia | 5 % |
| water | to make up to 100 % |

In situations when protective equipment, tools, or machine parts are to be decontaminated, or when the ambient temperature is freezing, there is advantage in adding an alcohol such as ethanol (industrial spirit), isopropanol or butanol to the formulation. Up to 50 % of solvent is recommended depending on the circumstances. The use of alcohols in the formulations means that the neutralizers will be flammable and that appropriate precautions will be necessary to avoid all sources of ignition or overheating.

Formulation 5

| | |
|--|---------------------|
| liquid/yellow soap (potassium soap with 15 % surfactant) | 2 % |
| polyethylene glycol (PEG 400) | 35 % |
| water | to make up to 100 % |

This is particularly useful for drums.

Key Theme 4: Using personal protective equipment

The polyurethane industry employs a wide diversity of processes and activities that demand different systems of control for minimizing exposure to MDI and TDI. In all instances the first priority should be to minimize exposure by the use of appropriate engineering measures, including enclosure and the provision of suitable ventilation, rather than to rely on personal protective equipment. **In workplaces in which engineering measures and adequate ventilation are provided, it should not be necessary for workers to use breathing apparatus and to wear protective clothing beyond that normally used in the general chemical industry.** When suitable engineering measures are not available, for example during some maintenance work or when spraying externally, the protective equipment will need to be matched to the expected diisocyanate exposure situations. It is important that protective equipment

- protects those parts of the body most liable to exposure, especially the lungs;
- is comfortable enough to be worn properly for long periods;
- provides adequate resistance to penetration (not necessarily perfect impermeability).

Personal protection needed for use with MDI or TDI can be selected from ranges of equipment already available to the chemical industry.

Normal operations

In many workplace environments, personal protective equipment will need to take account of the possibility of spills and splashes of liquid diisocyanates onto the skin or into the eyes and, if necessary, protection of the airways from inhalation of vapour or aerosol if engineering measures cannot be applied in a particular situation (API, 2001a, 2001b). Contaminated surfaces can also be a source of exposure to diisocyanates. Respiratory protective equipment will usually not be necessary in well-controlled workplace environments. However, when maintenance or repair work is taking place, those involved may require respiratory protection, unless it is known that diisocyanate exposure is below a concentration that may cause harm. Respiratory protection will be necessary when carrying out spraying operations externally, and also when spraying internally in the absence of proper spray containment and removal facilities. Respiratory protection should also be used when heating diisocyanates.

It is important to note that all the chemicals to which workers may be exposed in a particular workplace need to be taken into consideration when

selecting protective equipment. Chemicals that will often be found in workplaces handling diisocyanates are solvents, release agents, catalysts and chemicals provided for the neutralization of diisocyanates. Chemicals may well also be present for nonpolyurethane activities.

The selection of personal protective equipment depends on many factors such as:

- job demands (heavy or light wear, manual dexterity);
- degree of exposure (light or occasional, to severe);
- duration of exposure/wear time;
- physical fitness of the wearer.

Personal protective equipment must be in good condition. It should be noted that this equipment may deteriorate on storage or as a result of extended use. It may have been misused or subject to abrasion. As a result it frequently performs less effectively in practice than in laboratory tests. The reasons for the correct use of personal protective equipment may be forgotten, and care should be taken to ensure that best practices become commonplace.

In most workplace situations where care is taken to minimize exposure, the protective equipment that is necessary may consist of some or all of the following:

- | | |
|--------------------------|---|
| • body protection | overalls (coveralls); |
| • eye protection | safety glasses, face shield or goggles; |
| • hand protection | gloves; |
| • foot protection | boots; |
| • respiratory protection | breathing equipment. |

There may be a need to wear additional protective equipment other than that necessary for protection against chemicals. For example, safety helmets (hard hats) may be mandatory for certain jobs and it may be sensible to wear an impermeable apron if splashes are expected.

Emergency situations

Dedicated equipment for use in emergency situations must be in locations that are accessible, clearly marked and known to those who may have to use it. Since emergency equipment will be used only very infrequently, it is important that training is provided at intervals to ensure that workers remain competent in its use. Respirators for emergency use should be maintained regularly to ensure that they are fully functional at all times. There may be regulations defining the frequency of maintenance.

Escape from an incident

The main requirement is to provide breathing protection for a short period of time only. Cartridge respirators are suitable for *emergency escape*; the cartridges should be replaced after use since there can be no way of knowing the amount of diisocyanate that the cartridge has absorbed.

Key Theme 6: Dealing with accidents

Dealing with an emergency situation

Full protective equipment may be required in the case of even minor workplace incidents. For example, if a pipe leaks during unloading, then full protection will be needed (Figure 2.5). Full protective equipment will usually consist of:

- a chemical suit, or an impermeable overall with hood;
- impermeable gloves;
- impermeable boots;
- respiratory protection suitable for extended use, for example a positive pressure breathing apparatus with full face mask which is supplied by air cylinders.

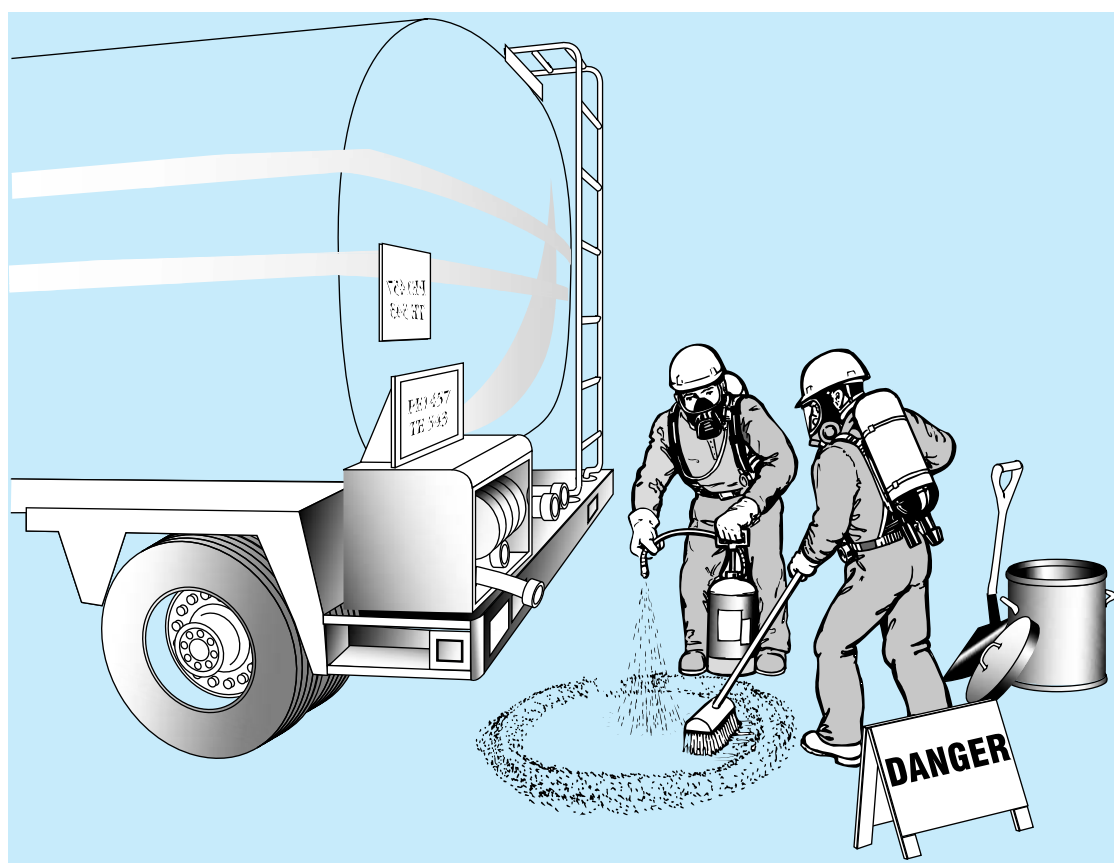


Figure 2.5 Dealing with a diisocyanate spillage

Selection of personal protective equipment

A choice of equipment is needed to allow for individual preference, personal fit (different makers use different standard sizing systems) and different demands of the job. Care should be taken to match the level of protection provided to the potential exposure to the chemicals. The training should particularly emphasize the importance of fitting the equipment to the person. Correct training should ensure that the wearing of personal protective equipment does not make the

worker think that he is safe in all situations. This can lead to unsafe practices which can be hazardous to the wearer and to other workers. The objective in selecting equipment is to provide acceptable and comfortable equipment with a reasonable degree of protection for short exposures, rather than excellent protection in equipment which is very uncomfortable and may even be discarded. Equally, it is unreasonable, and might introduce other risks, to expect a worker to wear heavy protective clothing, especially in hot conditions. In hot conditions some workers leave suits unfastened, or even tear out the sleeves. If the conditions of the plant are such that heavy equipment has to be worn for long periods during normal operations, it is an indication that the process needs better design.

An excessively wide range of available equipment options may increase the likelihood of mistakes in issuing equipment for specific jobs. Employers will not want to carry a wide range of equipment anyway, and will find it simpler to over-specify the protection needed for some jobs in order to eliminate some stock items. Where personal protective equipment is required and provided, it should not be just to the minimum theoretically required standard.

Air line systems, in which breathing air is supplied by lines throughout the factory, generally give a higher standard of respiratory protection than air-purifying respirators and, after the initial cost of the air distribution supply, they are cheaper to maintain and run. Powered cartridge systems cost more, and need more maintenance, than unpowered systems, but they are generally more comfortable and more likely to be worn correctly.

Protective clothing

Any protective clothing must be removed with care after use to ensure that the wearer does not become contaminated. Any contaminated items must be cleaned or disposed of safely.

Body protection

Long sleeved garments are preferred in order to protect the arms from skin contamination. Overalls/coveralls should preferably be made from heavy cotton or a laminated material and should provide protection to the wearer for more than 8 h. Many laminates of PVC, neoprene and polyurethane performed well in permeation and penetration tests with MDI and TDI, and uncoated materials were less effective. Solvents can affect permeation times markedly and diisocyanate may well be carried through the material with the solvent.

Disposable clothing suitable for the chemical industry, even if offering shorter protection times, is often preferred because of the difficulty of decontaminating other types of protective clothing. Garments which are provided with snap or VelcroTM-type fastenings allow fast removal of contaminated clothing in an emergency.

It may be thought that a full body suit in an impervious material would provide complete protection. However, this approach can be wrong on several counts. Almost no garment is fully impervious, and if it were the wearer would suffer heat stress. In practice, except in the most specialized air-supplied suits, air permeates through the fabric, leaks through the fastenings or is pumped by body movement in and out of cuffs at neck, wrist and ankle.

Permeation testing on protective clothing
SPI (1994a, 1994b); Robert and Hayward (1999); Robert *et al.* (2000).

Eye protection

Eye protection is often mandatory in the workplace to protect workers from a variety of hazards such as splashes from diisocyanates. Safety glasses, a face shield or goggles are normally adequate for light duties. The operator should wear a full-face breathing apparatus or air line hood if the job involves a high risk of splashing or releases of jets and sprays of liquid diisocyanates. Care should be taken to ensure that eye protection is not handled with contaminated gloves.

Hand protection

Hand protection may need to be worn in many operations to prevent contact with any contaminated surfaces. Care is required in choosing gloves appropriate to the job in terms of wear resistance and resistance to chemical contact. There are virtues in selecting robust gloves of moderate resistance to diisocyanates, and changing frequently to a new pair. Gloves have been tested for their resistance to diisocyanates. Information is available on a wide variety of glove materials and proprietary designs (SPI, 1994a, 1994b). Nitrile rubber showed excellent resistance to polymeric MDI and TDI; butyl rubber, neoprene and PVC were also effective. Natural rubber and polyethylene did less well, but were likely to be satisfactory for light, precise work of short duration. Light-duty nitrile rubber gloves allowed good manual dexterity. Solvents can significantly reduce the protective ability of gloves to diisocyanates (Robert and Hayward, 1999; Robert *et al.*, 2000). Diisocyanates can cause impervious coatings to harden and crack. Gloves should be replaced if this happens. The touching of unprotected skin with contaminated gloves can cause problems, and the source of such exposure is not always recognized.

Foot protection

Feet should be protected from splashing, and safety boots provide adequate protection on normal polyurethane processing plants. However, rubber boots may be more suitable for decontamination after spillages. Cost is not a reliable guide to durability or resistance to permeation by diisocyanates.

Respiratory protection

Air can be supplied to the user through full-face masks, half-masks, visors, hoods, helmets and blouses (half-suits). Specialist advice should be obtained in selecting the best form of equipment for a particular situation. Figure 2.6 illustrates the main types of respiratory protective equipment for diisocyanates.

The use of respiratory protective equipment must be considered in situations in which the levels of diisocyanate cannot be controlled to below the regulatory limits, for example during maintenance activities. Equipment for respiratory protection is covered by regulations in many countries, and these should be consulted if there is any doubt about equipment suitable for use with diisocyanates. There are well-developed standards for respiratory protective equipment in most parts of the world. They usually refer to sizing, fit tests, face seal leakage, construction and other general features. Performance tests

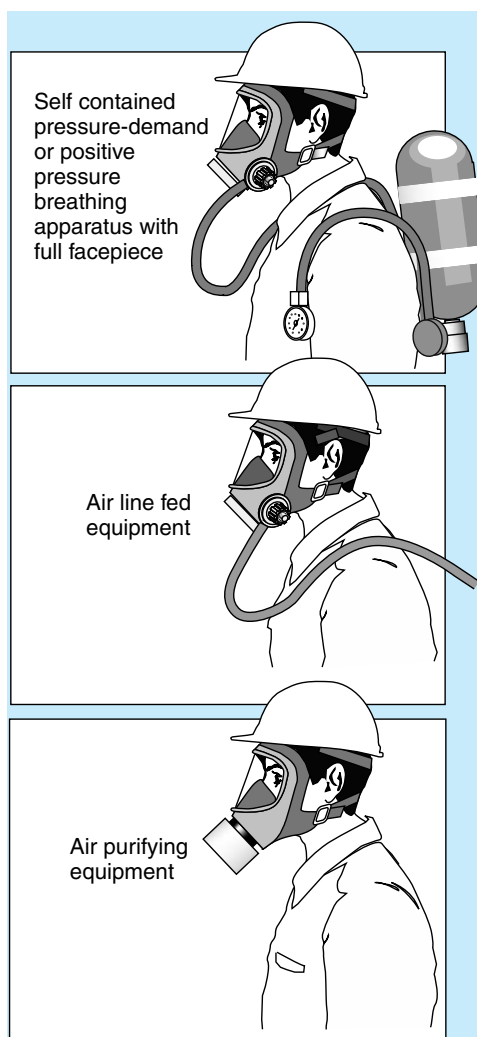


Figure 2.6 Types of respiratory protection

normally specify simple test substances which do not include diisocyanates. It is also necessary to consider the effect of airborne substances (in particular acid and solvent vapours) on the sensitive working parts, especially valves and seals that can harden or degrade in storage or use.

There are several studies indicating that much respiratory protective equipment can fall seriously short of the performance suggested by face-seal leakage tests or by tests on the filter cartridge alone. In most tests, the human subjects are selected to exclude those for whom a good face fit is difficult to achieve. The quality of fit may be important to performance. People do vary, however, and equipment will not fit all equally well. Where the tests include movement and speech, the tests are limited in duration and do not usually include severe bodily exertion or severe cross-draughts. Hence the quoted parameters (Total Inward Leakage, Nominal Protection Factor or Assigned Protection Factor) may not represent performance in practice, most commonly because

the equipment performs worse in practice than in the standard protocol in the test room. The degree of protection afforded by air-supplied or air-cleaning devices varies greatly (even several hundred fold) with the type of face piece.

Respiratory protection can affect visibility, both downward past the air mask and often to the sides; also communication can be difficult. A feeling of claustrophobia or confinement can affect some workers.

Equipment for respiratory protection in workplaces should be stored in a clean, dry, easily accessible area and should be subject to regular, periodic inspection and maintenance to ensure that it is fully functional at all times. Training and refresher training in the usage of the equipment is necessary because the equipment may be used only very infrequently.

Some masks give no protection

Simple gauze or thin paper masks ('nuisance dust masks') that are commonly available to reduce the level of particulates breathed in offer no protection against diisocyanate vapour and aerosols. They must never be used to protect against airborne MDI or TDI.

Respiratory protective equipment falls into two categories (Figure 2.7):

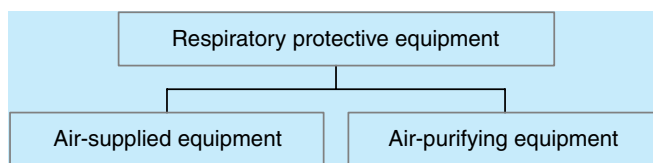


Figure 2.7 Major classes of respiratory protective equipment

- Air-supplied equipment provides uncontaminated breathing air from an air line or a cylinder.
- Air-purifying equipment cleans the atmosphere before supplying it to the wearer. Renewable cartridges (also known as canisters) perform the cleaning.

Air-supplied equipment

There are many types of air-supplied equipment (Figure 2.8). Some regulators specify air-supplied equipment with full face piece, operated in a positive-pressure demand mode, or air-supplied face piece, helmet or hood, operated in a continuous flow mode for use with diisocyanates. The air may be supplied through an air line or may be supplied from cylinders in self-contained equipment. These systems can restrict movement and air lines may provide a tripping hazard. There is usually no means of warning the wearer if the air supply fails for any reason.

Fresh air hose supplied systems comprise a mask with a trailing wide-bore tube. However, it may be difficult to know whether the intake of the tube is drawing in clean air. Supplied compressed air is usually preferred as the quality

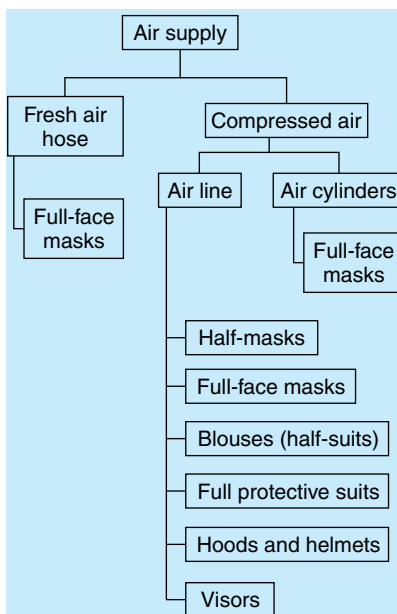


Figure 2.8 Sources of air supply in air-supplied equipment

can be better controlled. For jobs in which great mobility from a compressed air supply point is not required, a trailing uncoiled hose delivering compressed air to a hood or full-face mask is satisfactory. Although coiled air lines look neater, they may be subject to tangling. Cylinder fed breathing equipment should be available (Figure 2.9) for use as emergency breathing equipment, for example, for cleaning up large spills and for fire fighting. This specialized equipment is heavy and personnel training is required before it can be used. Cylinders have a limited supply of air and cannot be used over long periods of time. Some standards are available on the quality of air suitable for use with breathing equipment (for example, see US OSHA Respiratory Protection Standard 1910.134). It is imperative that normal factory compressed air, which may contain oil droplets, should not be used.

Examples of suitable air line fed equipment are shown in Figure 2.10. Both air line and cylinder supplies can be used to provide air to the wearer either as a constant flow, or on demand.

- **Constant flow.** A constant flow of air is simple to provide and use, but results in a large air usage. Cylinders are very rarely suitable for the provision of constant flow air, as their contents are soon exhausted. Constant flow systems include full-face mask, hood, blouse or ventilated visor types. The extensive gaps around a visor make this type suitable only for low risk work.
- **On demand.** Positive-pressure demand equipment is based on a tight fitting face piece, inside which a pressure slightly above atmospheric is maintained. When the wearer inhales, the demand valve opens before the mask pressure drops to atmospheric. Equipment of this type should be used whenever the highest standard of protection is needed. Negative-pressure demand equipment, in which the valve does not open until the mask pressure is reduced below ambient pressure by inhalation, may allow the possibility

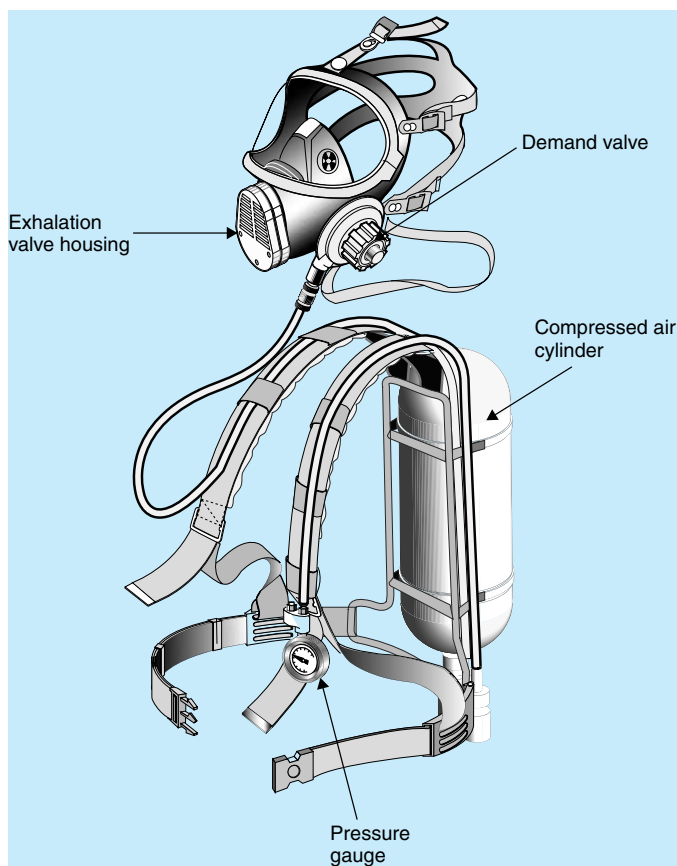


Figure 2.9 Self-contained breathing apparatus (SCBA). Adapted with permission from *Respiratory Protective Equipment: a Practical Guide for Users* (UK HSE, 1990)

of inward leakage. Air-supplied constant flow systems, or positive-pressure demand valve systems, should always be used for spraying when there is no engineering control of aerosols.

Air-purifying equipment

This type of equipment incorporates air-purifying cartridges, but has no independent air supply. According to the design, the cartridge may remove from the surrounding atmosphere vapours, or particulates including aerosols, or both vapours and particulates together. The cartridges tend to be very efficient at absorbing vapours or particulates until their capacity is exhausted and breakthrough occurs. Contrary to general expectations, gas-absorbing cartridges are not necessarily efficient at removing particulates, and particulate-filtering devices may not be efficient at removing gases. Dual function cartridges that absorb both gases and particulates are available and are most likely to be suitable for use in the presence of diisocyanates.

Equipment that relies on cartridges to purify the air has a serious limitation. In currently available equipment of this type, there is no end-of-service-life indicator for warning the wearer that the filter cartridge or canister is no

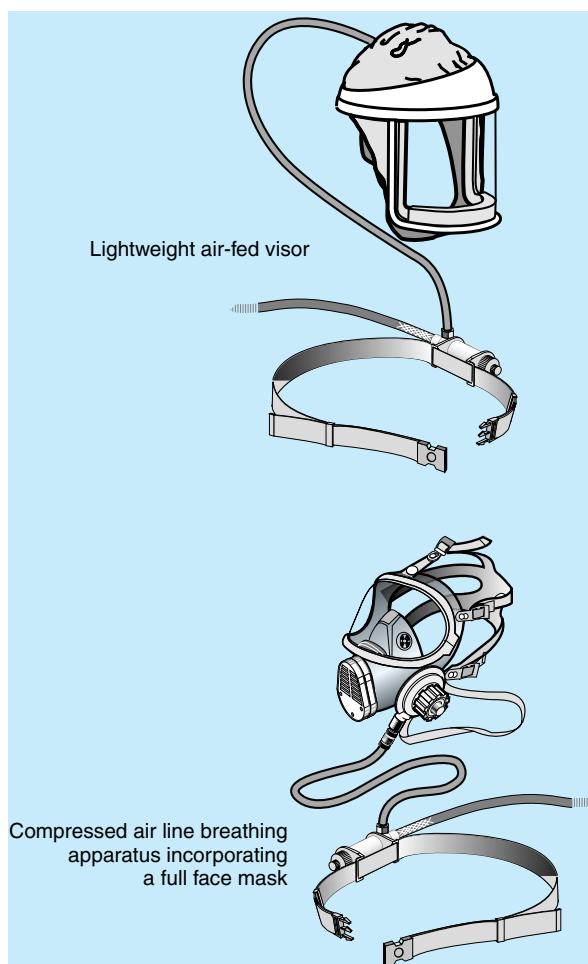


Figure 2.10 Air line fed breathing apparatus. Adapted with permission from *Respiratory Protective Equipment: a Practical Guide for Users* (UK HSE, 1990)

Cartridges and filters: gases and aerosols

Gases and aerosols behave in different ways, and need to be removed from breathing air in different ways. A cartridge containing carbon granules is used to remove potentially harmful vapours. As the air passes easily through the cartridge, vapours such as MDI or TDI diffuse very rapidly onto the carbon, to which they adhere. Aerosols do not diffuse quickly and pass through the spacious air channels with the air flow. A filter is used to capture the aerosols. The filter comprises a thin mat of fibrous material that offers little resistance to the breathing air flow, but provides a labyrinthine or tortuous route for the air. The aerosols, which have much greater momentum than individual gas molecules, are deposited on the fibres as the air flow changes direction.

longer effective for diisocyanates. Odour cannot be used as an indicator as the wearer cannot smell MDI or TDI until the concentration is greatly in excess of permitted levels. Users of cartridge-containing respiratory protective equipment should understand that any abnormal odour or irritation is evidence that the capacity of the cartridge is very much overloaded and should have been replaced earlier. The recognition of such warning properties must, however, **never** be relied upon as the mechanism for determining when a

cartridge should be changed. Effective change schedules must be established

and implemented by the employer. The employer may obtain relevant information from cartridge suppliers and other experts. It may be possible to use data that have been determined by experimental work including 'breakthrough time' studies, by mathematical predictive modelling and by workplace simulations. Whichever method is selected, the employer must implement a regular cartridge change schedule based on the best information available (OSHA, 1998). Great care should be taken to ensure that the use of cartridges is confined to short periods of time before they are changed, unless the life expectancy of the cartridge in that particular workplace situation has been established. The local regulatory situation and the potential exposure to a range of chemicals will need to be considered in selecting cartridge-type respiratory protective equipment.

Cartridges are usually colour coded to distinguish the suitability for removing different classes of contaminants, for example organic vapours, ammonia and organic amines, and particulates, including aerosols. Cartridges that are suitable for removing diisocyanates are not usually identified as being solely for that purpose. Cartridges are nevertheless available that are suitable for diisocyanate vapours, diisocyanate aerosols and for a combination of both vapours and aerosols. The nomenclature for air purifying cartridges is not standard across the world, and local advice must be sought if there is any doubt concerning the correct cartridge or canister to be used. Further information is available from manufacturers and regulators.

Cartridge-containing equipment falls into two classes, those that are lung-powered and those that have motor-driven pumps to pull the air through the cartridge (Figure 2.11).

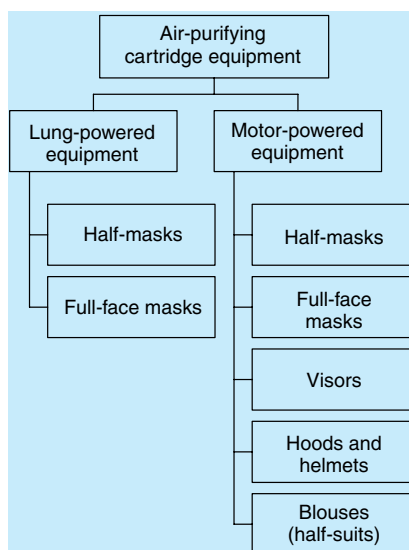


Figure 2.11 Types of cartridge-based respiratory equipment

Lung-powered respirators may employ a half-face mask, covering only the nose and mouth, or a full-face mask offering protection to the eyes also (Figure 2.12). Lung-powered systems tend to be exhausting to wear for long periods.

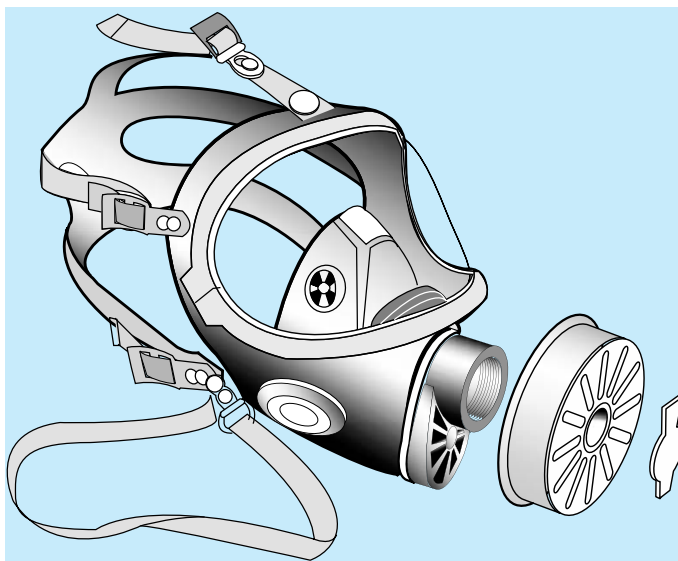


Figure 2.12 Lung-powered full face mask cartridge respiratory equipment. Adapted with permission from *Respiratory Protective Equipment: a Practical Guide for Users* (UK HSE, 1990)

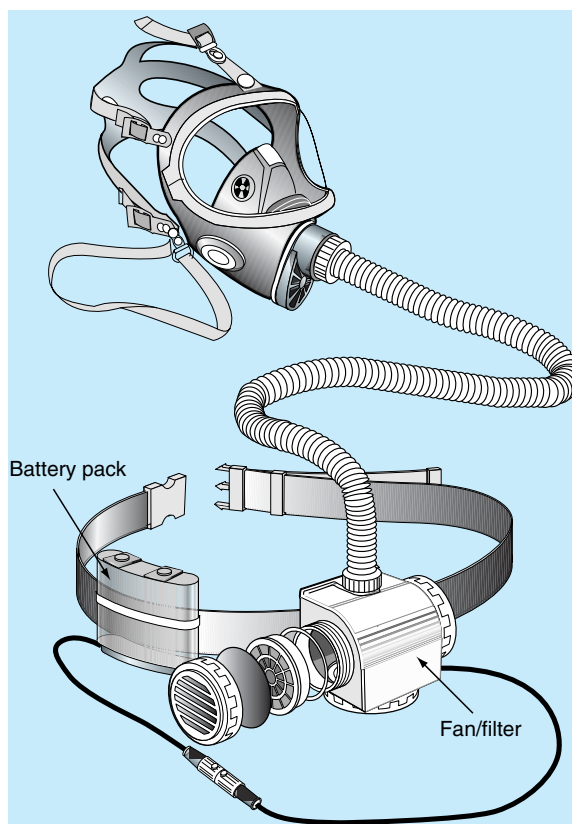


Figure 2.13 Motor-powered full face mask cartridge respiratory equipment. Adapted with permission from *Respiratory Protective Equipment: a Practical Guide for Users* (UK HSE, 1990)

Motor-powered versions (Figure 2.13) operate by pumping filtered air to the wearer. Motor-powered respirators offer more versatility in face/head cover such as:

- lightweight visor;
- visor combined with safety helmet;
- hood;
- blouse (half-body, face and head protection).

The effectiveness of some typical air-purifying respirator cartridges in removing MDI aerosols from air has been investigated. Organic vapour cartridges without a particulate filter were not effective at removing MDI aerosols from air, whilst organic vapour cartridges with filters for dusts/mists and high efficiency filters (HEPA) removed more than 99 % of MDI aerosol and vapour in all the atmospheres tested (Spence *et al.*, 1997). Low breakthrough times of very fine MDI aerosols were found with those cartridges that were not designed to remove particulates (Table 2.4). Cartridges from different manufacturers did not necessarily have equal efficiency at removing very small particles. Interestingly, in this study the formation of MDI aerosols was evident even at very low ($<100 \mu\text{g}/\text{m}^3$) total MDI concentrations.

Table 2.4 Cartridge breakthrough testing with spray-generated MDI aerosol.

| Source of cartridge | Cartridge type | Breakthrough time min |
|---------------------|--|--------------------------|
| Manufacturer 1 | Organic vapour/high efficiency particulate | >1440 |
| Manufacturer 2 | Organic vapour/dust/mist | >1440 |
| Manufacturer 1 | Organic vapour/dust/mist | 200 |
| Manufacturer 1 | Organic vapour | <10 |

Aerosol test atmospheres: 5300 to 9000 (mean 7300) $\mu\text{g}/\text{m}^3$; mass median aerodynamic diameter = $2 \mu\text{m}$.

Breakthrough time was defined as the time taken to reach a concentration of 1 ppb MDI.

Key Theme 5: Monitoring exposure

Why monitor levels of diisocyanates?

There are several reasons why a monitoring programme should be established in any workplace or site using diisocyanates:

- to ensure that workplace controls are fully operational and employee exposure is identified and minimized;
- to ensure that any releases from the site are identified and, when necessary, any exposure of the community and environment is controlled or eliminated;
- to demonstrate compliance with regulatory requirements.

What needs to be monitored?

In order to fulfil the norms of product stewardship and regulatory compliance, it may be necessary to monitor the following scenarios.

The workplace

- exposure of process workers, maintenance personnel, other workers and visitors;
- changes of worker exposure with changes in workplace or process conditions;
- surface contamination;
- exposure during and after spillages.

The community and the environment

- stack release levels;
- fenceline concentrations;
- exposure during and after spillages due to transport accidents.

Furthermore, it will be necessary to have programmes for the regular calibration of analytical equipment.

How should monitoring be carried out?

The choice of a method of monitoring for MDI or TDI depends on a number of factors, and selection of the method should always be undertaken with professional advice. A range of techniques is available for sampling and analysis of diisocyanates, but all have limitations on their use. Knowledge of the situation in which monitoring is to be carried out is essential before a choice can be made. Determination of exposure depends on both representative sampling and reliable analysis. Representative sampling depends on the sampling strategy, on the positions at which sampling is carried out and on the correct use of the sampling device itself. Further details on the strategy of sampling will be found below in *Part 2, The workplace: storage and use of MDI and TDI*. The analytical methods, and the factors which must be taken into account in making the choice, are discussed in *Part 5.7, Sampling and analysis*.

Factors that affect the choice of method include:

- *The physical form of the diisocyanate.* Depending on the nature of the operation in the workplace, a diisocyanate may be present in the atmosphere as vapour, aerosol, or both, or even as a reacting mix with polyol blend. If the samples of aerosols or vapour are not representative of what is present in the air, the final result will not give an accurate indication of the exposure levels.
- *The reason for which the monitoring is being undertaken.* For example, if the purpose is to determine workplace exposure levels, it is important that the monitoring reflects as closely as possible the actual levels experienced by personnel. Concentrations of diisocyanate in the workplace can vary considerably if there are air currents, and during certain steps in a routine operation, for example during mould closure. There needs to be a clear

understanding of the difference between the results obtained from workplace area monitoring (static monitors) and those from personal sampling devices which sample the atmosphere in the breathing zone of the worker.

- *Sampling conditions.* Measurement of diisocyanate releases within an exhaust stack must take into account factors such as other substances present, air speed, temperature and humidity.

Regulatory authorities differ in their requirements for the measurement of diisocyanate levels in the workplace. Some specify the limits to be achieved as concentrations of MDI or TDI. Other authorities express the limits in terms of the total reactive isocyanate group (TRIG) concentration (see *Part 5.6, Occupational exposure limits, stack limits and community limits*).

- *Local regulatory requirements.* There may be requirements as to the method used to show compliance with occupational exposure limits or to determine releases from polyurethane production plants. It may be possible to use a method other than the recommended one if the chosen method can be shown to fulfil regulatory requirements.
- *The technical skills available.* Some monitoring instruments can be operated fairly simply with little training required, while other methods require a high level of analytical equipment and professional expertise. A combination of methods of differing complexity, such as continuous paper tape monitoring combined with a regulatory reference method, may be required to give a complete picture of exposure levels.

When should monitoring be carried out?

A regular programme of sampling and analysis should be established to build up an understanding of the exposure of the workforce. The strategy for this is discussed below in *Part 2, The workplace: storage and use of MDI and TDI*. An alarm system based on continuous monitoring to detect raised levels of airborne diisocyanates may be set up to cover areas of the plant where, for example, high levels could be released if the ventilation failed.

It is essential that monitoring be carried out routinely and whenever

- a new process is established;
- there have been changes to existing equipment or to a process;
- health problems are suspected;
- a leakage is suspected;
- there has been a spillage or other incident involving release of diisocyanate, to check the atmosphere before personnel can return to the area.

The establishing of a monitoring strategy will depend on the process and on regulatory requirements. Different monitoring equipment may be needed for recording the different types of exposure levels. Advice on sampling and analysis is available from diisocyanate suppliers, specialist analytical services, local regulatory authorities or instrument manufacturers.

Record-keeping is an essential part of all monitoring. Information should be logged on the date and time, the method used for monitoring, the position of the sampling, as well as the values obtained. Information from personal monitoring

must indicate the individual involved and the jobs being undertaken. There needs to be an understanding of the relevant regulatory demands, which may include statutory recording formats for the results of workplace monitoring.

Key Theme 6: Dealing with accidents

Accidents can happen

Accidents can happen even in the best-managed operations. Spillages occur from a variety of causes, and very occasionally incidents arise involving the development of excess pressure in containers. Major accidents involving MDI or TDI are fortunately very infrequent. It is, nevertheless, important to have procedures in place to deal with all these eventualities, however unlikely they may be. It is necessary for all staff to receive periodic training on the correct procedures to implement, and to be aware of the possible health implications of over-exposure to diisocyanates.

Most workplace releases of diisocyanates involve relatively minor spillages or drips of diisocyanates that will be neutralized by the production or maintenance staff involved. There should always be easy access to an adequate supply of neutralization materials available in workplaces and the location of these materials should be clearly displayed. Supervisors should ensure that all incidents, however minor, are recorded so that procedures can be analysed and where necessary modified, or refresher training undertaken, to prevent recurrence. Supervisors will also need to be aware of the possible delayed health effects that may occur if over-exposure has arisen.

In many organizations it will be necessary to have a designated emergency team which is able to take control in the event of a larger accident. The team should have links with the local emergency services who need to be aware of the location of storage vessels containing diisocyanates and other chemicals. Contingency procedures for the containment and neutralization of spills need to be discussed with them in case their help is required at any time. The diisocyanate suppliers offer specialist advice and practical help in many emergency situations, and have mutual aid networks in some countries to give help and advice during an emergency. These services can be accessed at any time of day or night through telephone numbers given in the manufacturers' safety literature. See *Part 2, Transport of MDI and TDI* below for further details.

If the accident results in an individual breathing airborne diisocyanate, or if the person receives splashes on the skin or in the eyes, the first aid procedures summarized below should be followed. The background to these procedures is discussed in *Part 3*. First aiders need to remember that exposure of themselves may still be a possibility and they may need to wear protective equipment before helping others. If a local physician is called in to attend to an affected individual, or if hospital treatment is required, it is important that relevant information is provided to the medical staff. Ideally, the manufacturer's safety data sheet should be made available.

MDI or TDI: First aid

Breathing difficulties due to vapour, aerosol or MDI dust

- The person affected should be moved from risk of further exposure and made to rest.
- Obtain medical attention immediately.
- The onset of symptoms may occur several hours after exposure has taken place.

Eye contamination

- Flush the eyes immediately with the contents of several sterile eye wash bottles or copious amounts of tap water. Then remove contact lenses, if present and easily removable, and continue eye irrigation for not less than 15 minutes.
- Obtain medical attention.

Skin contamination

- Wash off thoroughly with large amounts of water and then wash well with soap and water.

Swallowing

- Do not induce vomiting.
- Wash out the mouth with water.
- The person affected should be made to rest.
- Obtain medical attention.

Note for guidance of physicians

- MDI and TDI are respiratory irritants and potential respiratory sensitizers. There are no specific antidotes and treatment is essentially symptomatic for primary irritation or bronchospasm.
- MDI and TDI have very low oral toxicity.
- Post-incident checks are needed.

Spillages

All spillages, however small, must be attended to immediately since there is a risk of over-exposure of those nearby. Most spillages involve relatively small quantities of diisocyanates and arise, for example, from accidents during the maintenance of equipment or from a drum damaged during handling operations. Much larger quantities may be released if a feed line bursts. Storage tanks may occasionally be overfilled, resulting in spillages, and hoses used in the transfer of diisocyanates may become uncoupled. Transport accidents can release large quantities of diisocyanates, and these can, of course, occur in situations far removed from a factory environment and experienced help

may not be available. In all situations, the actions that should be taken are essentially the same.

The principles to be adopted should be to protect people first, then to prevent or minimize any releases to the environment, and finally to protect property and product.

1. Identify the material(s) involved.
2. Evacuate from the immediate area everyone not essential to dealing with the emergency and keep them upwind to avoid breathing vapour. Isolate the area and prevent access. Remove ignition sources.
3. Notify the local emergency services and the management immediately if the spill cannot be handled by the available personnel. Call the supplier or the emergency response number provided by the supplier for expert help if needed.
4. Put on full personal protective equipment (suitable respiratory protection, face and eye protection, protective suit and gloves).
5. Control the source of the leak, where applicable. This may involve actions such as closing a valve in a supply line, or undertaking an emergency repair to a hole in a drum with a temporary bung or suitable adhesive tape.
6. Open doors and windows, if inside a building, to increase the ventilation and aid removal of diisocyanate vapours.
7. Contain the spill to prevent further spread of diisocyanate, when possible also absorbing the diisocyanate with sand, wet earth or absorbent clays (vermiculite or kieselguhr). Add neutralizer to the absorbent materials. Pump (using a drum pump) any diisocyanate liquid standing in pools into closed, but not sealed, containers that are clean and dry. Spill pillows can be used for containing big spills. If the spillage is very extensive, cover the spillage with fire fighting foam (for example 3 % protein) to minimize the liberation of vapour. Whenever possible, prevent the material from entering waterways or drains, including lakes, rivers, streams and sewers. If this happens, notify the water authorities immediately.
8. Neutralize the diisocyanate and decontaminate all surfaces and equipment that have been in contact. The procedures and formulations in *Key Theme 3: Neutralization, decontamination and disposal of wastes* should be used. Isolate the residues for safe disposal.
9. Check, using analytical equipment, that the clean-up procedures have been effective and that decontamination has been successful. If the diisocyanate has been in contact with a porous surface, or one with cracks or fissures, the decontamination procedure may not have been fully effective. If the spill occurs on a bitumen surface there may be some damage requiring repair. There may be a slow release of further diisocyanate that will require additional attention, for example by covering with impermeable sheeting on top of a thin layer of further wet absorbent. Solidified diisocyanate may be removed mechanically, including the use of sandblasting. If sandblasting is used, the contaminated sand must be collected, decontaminated and disposed of in an approved manner.
10. Remove waste materials for incineration, for disposal by a specialist contractor or for landfill on approved sites. The choices will probably be governed by local regulations.

11. Make a record of all accidents, and consider actions to prevent recurrence. Actions may include amendment of working procedures, improvement of equipment and machinery, and improved training of those involved.

Actions following a spillage

- remove nonessential personnel;
- inform management;
- put on protective equipment;
- contain spillage;
- neutralize diisocyanate;
- decontaminate surfaces;
- isolate and dispose of waste;
- monitor for residual diisocyanate;
- record what has happened; take steps to prevent recurrence.

Emergency equipment

- personal protective equipment;
- neutralizer;
- empty drums;
- absorbent material;
- shovel and brush;
- adhesive aluminium tape;
- labels;
- bungs;
- equipment to monitor for diisocyanate.

Contamination of eyes, skin or hair by diisocyanate

See the *First Aid* advice for eye contamination. The key consideration is speed.

Do not use any neutralizer solution in the eyes. Any splashes of diisocyanate on the *skin* should be removed as soon as possible by wiping with absorbent material, followed by washing with soap and warm water. Contaminated clothing must be removed and decontaminated as described in *Key Theme 3*.

Study on skin decontamination

A study on removing polymeric MDI from the skin has shown that water or soap and water were less effective than corn oil, polypropylene glycol (molecular weight about 700), or a commercial polyglycol-based skin cleanser (Wester *et al.*, 1998). Water, or soap and water, were decreasingly effective with time. Therefore cleaning soon after contamination is important.

If spillage of a diisocyanate onto the skin is not removed quickly it will react with water in the skin, and possibly with the skin itself, leaving a leathery deposit which cannot be easily removed. The deposit will come off mechanically in due course. It is important to use cleaning materials that will not cause the diisocyanate to pass

through the skin. Many organic solvents, such as dimethylsulphoxide (DMSO), dimethylformamide (DMF) and acetone, will dissolve MDI or TDI. However, **they should not be used for skin cleansing** because they may cause

permeation of the diisocyanate into or through the skin and may have toxic or defatting actions of their own. Proprietary skin cleaning agents may be used, but only if hygiene studies have shown them to be effective. Proprietary skin hygiene packs may contain both 'indicator' wipes to check whether the skin is contaminated, and neutralizer solution to clean contaminated skin.

Dealing with contaminated skin

Minor splashes

- Remove contaminated clothing.
- Clean off excess diisocyanate from the skin immediately using dry towels or other absorbent fabric. Then wash with clean warm water, or with a proprietary cleaning agent.

Drenching

- Remove contaminated clothing.
- Shower without delay using soap, or a proprietary cleaning agent, to wash off the diisocyanate. Do not remove respiratory protection (if worn).
- **DO NOT USE organic solvents or alkaline neutralizers.**

If hair becomes contaminated with diisocyanate, towels should be used to absorb as much of the material as possible. The hair should then be washed thoroughly with warm water. Mineral oil and/or petroleum jelly may aid the removal of the diisocyanate. Any residual material may need to be removed by combing and possibly cutting off hair.

Further information on the effects of diisocyanates on the respiratory tract, the skin and the eyes can be found in *Key Theme 2: Protecting health* and in *Part 3, Health*.

Contamination of clothing

If clothing becomes contaminated following accidental release of diisocyanates, steps must be taken to avoid inhalation of vapours and to minimize transferring diisocyanate to the skin or eyes. If the person wearing the contaminated clothing requires first aid or medical attention, the helpers must avoid becoming contaminated themselves and must avoid breathing diisocyanate vapour.

Contaminated absorbent clothing should be removed carefully, avoiding spreading diisocyanates to the face and minimizing diisocyanate inhalation. If the person is wearing respiratory protection this should not be removed until cleaning is complete. If the clothing is impermeable to diisocyanates, for example a protective overall/coverall, showering should take place with the clothing and respiratory protection (if worn) left on. This will help to remove the diisocyanate and will minimize skin or respiratory contamination. If the shower is situated outside, steps should be taken to prevent it freezing in winter.

It is also important to note that TDI will crystallize if the water temperature is below 10 °C (50 °F), making its removal more difficult. Contaminated clothing should be put into impermeable bags or containers prior to decontamination, and before laundering or disposal (see *Key Theme 3: Neutralization, decontamination and disposal of wastes*).

Modelling spillage scenarios

Modelling, using realistic assumptions for temperatures and weather conditions, has been used to estimate diisocyanate concentrations in accidental releases scenarios. Modelling by Robert and Roginski (1994) shows that concentrations of MDI equivalent to 20 ppb are confined to the atmosphere directly above the spill. Because of its higher vapour pressure, TDI gives rise to concentrations well in excess of 20 ppb some distance from the spill.

A different modelling exercise developed the following scenarios.

Scenario 1

A hose ruptures when transferring MDI from a truck into a storage tank. The flow is 15 m³/h (approximately 4000 US gallons/h) at a temperature of 30 °C (86 °F) and the release continues for 5 min. The diisocyanate forms a pool 2 mm (0.08 inches) deep and 625 m² (6700 ft²) in area.

Result: Because of the low vapour pressure of MDI at 30 °C, concentrations of 20 ppb are confined to the atmosphere directly above the pool.

Scenario 2

A 200 litre (55 US gallon) drum of TDI falls from a truck and has ruptured. The temperature of the liquid is 30 °C. The liquid covers an area 100 m² (approximately 1000 ft²) at a depth of 2 mm (0.08 inches).

Result: A concentration of 20 ppb of TDI could be attained at ground level 90 m (approximately 300 ft) from the spill.

Examples of major accidents and their consequences

Two case histories of major spills of TDI and one involving polymeric MDI are given below. It will be noted that no long-term adverse environmental effects were produced. A full discussion of the absence of significant long-term environmental impact from the diisocyanates on plant and aquatic life can be found in *Part 4, The environment*.

Case history 1. Spillage of TDI from a road tanker

A road tanker containing 20 tonnes (44 000 lb) of TDI left the road, ran down an embankment and overturned. A valve was fractured and about 14 tonnes (30 000 lb) of material spilled from the tank before the leak could be stopped by the fire services. The remaining TDI in the tanker was pumped out by the haulage company, and the vehicle was decontaminated and removed.

The spilled material had spread out over an area of approximately 300 m² (approximately 3000 ft²) of marshy woodland, through which ran a water ditch.

The TDI was prevented from entering this ditch by the digging of a barrier ditch 1.5 m deep (approximately 5 ft), which was lined with polyethylene sheeting. The soil temperature of 5 to 10 °C (41 to 50 °F) caused the TDI to crystallize after a short time. About 12 h after the accident an operation was started to cover the area of the spillage with wet sand to a depth of 80 to 120 cm (approximately 31 to 47 inches). Most of the surface water and TDI was absorbed by this covering layer, which was mixed mechanically. The layer of sand and soil was not removed from the area in order to prevent possible contamination of the road surface by leaking TDI from the absorbent during transportation.

Samples of soil and water were taken from various points in the spillage area, to measure the concentrations of TDI present. One week after the incident TDI was detectable in the soil samples, but after 6 weeks the TDI had largely reacted with the water. Samples taken one year later contained no detectable TDI or TDA (toluene diamine). The ground water was sampled over a period of 5 years. No TDI or TDA was ever detected. Three months after the accident the vegetation was developing normally.

Case history 2. Spillage of TDI during the unloading of a ship

A spillage of 40 tonnes of TDI occurred at a dock during the unloading of a ship. As the ambient temperature was –20 °C (–4 °F), the TDI solidified and there was no pollution of the water. The TDI, mixed with the surface layer of ice and soil, was mechanically shovelled into containers. The spillage area was covered with clean sand.

Neutralization of the TDI was carried out in a mobile cement mixer using aqueous ammonia before the ambient temperature rose. Neither TDI nor TDA could be detected in the residues after this treatment.

Case history 3. Spillage of polymeric MDI during a rail accident

A train derailment involving several train tank cars resulted in a bridge failure. A rail tank car containing polymeric MDI was damaged and 50 tonnes of the diisocyanate were released, mainly into a river but also onto soil. A major fire lasting 2 days occurred which involved the contents of some other tank cars. The MDI did not ignite. The river water was at a temperature of 4 °C (39 °F) at the time of the spill, and 20 °C (68 °F) after 12 weeks. The MDI solidified into partially-reacted floating lumps and sheets of polyureas, which were recovered from the river by a floating barrier across the river and other means. MDI also collected on the river bed in areas of slow moving water. Material that was collected from the river, together with contaminated soil, was removed from the site and incinerated. About 18 h after the spill, 20 ft (6 m) downwind, levels of airborne MDI vapour were 2 to 4 ppb. The US Environmental Protection Agency declared the material in the river to be *nonhazardous* 3 days after the accident.

Development of excess pressure inside containers

Excess pressure may arise in containers or storage vessels containing MDI or TDI due to contamination of the diisocyanate. If diisocyanate in a closed container such as a drum becomes contaminated with water, the reaction of water and diisocyanate produces carbon dioxide, resulting in a build-up of pressure.

MDI and TDI react with water with the liberation of carbon dioxide gas. As both diisocyanates are immiscible with water, the rate of the reaction is slow when a two-phase system is present. The liberation of carbon dioxide will be much faster if the diisocyanates are finely dispersed, if there is a catalyst present (such as a tertiary amine or an alkali) or if a homogeneous mixture exists (e.g. when a common solvent is present). Liberation of carbon dioxide can occur in homogeneous, catalysed mixtures within seconds.

The excess pressure can cause the contents to be ejected in a vigorous stream or fountain when the container ruptures. Incidents have even been recorded in which bulging drums of diisocyanate have been propelled many metres with great force by the sudden release of pressure following drum failure. The best method for relieving

pressure in bulging drums will depend on the local situation. Chemical suppliers often have information on appropriate means of achieving this and should be contacted when establishing the safety procedures on a site.

If a package is bulging because of excess internal pressure immediate action should be taken as indicated below.

For drums under low pressure (a slight bulging of the face of the drum to below the level of the top rim):

1. Wear personal protective equipment including full face, eye and respiratory protection.
2. Slowly unscrew the bung to release pressure.
3. Advise the supplier of the problem, particularly the condition of the seal on delivery.

For drums under high pressure (face of drum bulging above the top rim):

1. **Do not attempt to release the bung.**
2. Clear everyone from the area.
3. Wear emergency protective equipment.
4. Cover the drum with tarpaulins or other material.
5. Isolate the drum if this is possible without risk. Care is needed as movement may agitate the contents and accelerate the reaction.
6. Contact the supplier for advice, or puncture the drum to release the pressure.

A drum can be punctured near its top and above the level of the liquid in the drum by means of a long lance or spike. A suitable device is shown in Figure 2.14. Detailed advice on how to undertake this operation will be available from the supplier of the diisocyanate. Whilst this operation is being carried out, all noninvolved staff must be evacuated from the area. Personnel involved must wear full protective equipment.

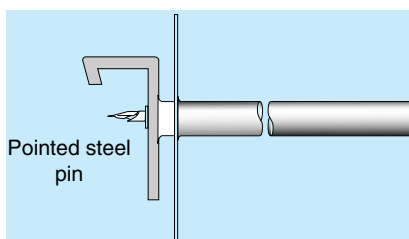


Figure 2.14 Drum puncturing device

The punctured drum must be placed in a controlled area until any reaction has finished, before being returned to the supplier as soon as possible for safe disposal. For transport, the punctured drum should be placed inside an overpack drum fitted with a pressure relief device. Further pressure build-up must be avoided by regular venting.

If drums fall into water during an accident they should be inspected after recovery for leaks. In the absence of leaks they should be wiped dry and returned to the supplier. Damaged or leaking drums must be suspected as potentially contaminated with water, with the consequent possibility of a pressure increase. A ruptured or leaking drum should be turned so that its damaged area is facing upwards. The drum should be covered to prevent the entry of rain, dirt or other materials. Air-inflated compression belts may be used as temporary seals for split drums. Holes should be sealed temporarily using a resin-based metal repair kit or a wooden plug. Any spillage should be removed and neutralized. The diisocyanate in the drum should be pumped or drained into a clean, dry, undamaged drum. The damaged drum should then be decontaminated before disposal.

If there is a leak in a stationary container such as a storage tank, it should be patched temporarily, for example with adhesive tape. The contents should be transferred to a container, which should be blanketed with dry air or nitrogen. The new container should be monitored to ensure that no excess pressure develops from any moisture.

Very serious situations may occur if a polyol is inadvertently discharged into a diisocyanate storage vessel, or vice versa. If this occurs, an emergency situation should be assumed to exist. The area should be evacuated, all stirring and circulation pumping stopped, the emergency services and the management called, and the suppliers consulted. It will be important to vent the vessel and to keep the contents as cool as possible until it is judged that no further reaction will occur. This may take many days. Once this situation is reached, further steps will depend upon the nature of the reaction mass inside the vessel. Specialist advice may be required from the chemical suppliers to effect satisfactory neutralization and decontamination procedures.

Incidents involving fire

MDI or TDI are not easily ignitable but may be involved in a fire caused or propagated by other materials. For polyurethane production facilities, the fire emergency planning and the precautions taken will depend very largely on factors such as the type of buildings and the overall fire load. Emergency planning and fire precautions as they relate to the handling of personnel, the involvement of the local fire service, and the location and type of alarms, are based on a risk assessment of the whole facility, and so are beyond the scope of this book. The following information is specific to MDI and TDI.

Fire behaviour and fire properties of MDI and TDI

A review of reports on some 400 incidents involving MDI and TDI over 30 years indicates that in no case has an incident been attributed to the ignition

Detailed information on incidents, fire properties and fire behaviour is given in *Parts 4, 5.4 and 5.5*, respectively.

of MDI or TDI, nor is there evidence that either has contributed to the propagation of the fire in any significant way.

The flash points and autoignition points of MDI and TDI are relatively high, and neither shows explosive properties, reflecting the difficulty of igniting these materials.

There are other aspects of fire which have to be assessed, and classifications of fire hazard have been introduced by a number of authorities. One scheme is that of the widely referenced US National Fire Protection Association (NFPA). This addresses the *health, flammability, instability and related hazards* that are presented by short-term exposure to the diisocyanates under conditions of fire, spillage or other emergencies. The proposed ratings for polymeric MDI, pure MDI and TDI (Collins *et al.*, 2000) are given in Table 2.5. NFPA has indicated that the interaction of diisocyanate with water *is not a significant hazard in a major fire situation*. This is an important aspect of extinguishing fires, as indicated below.

Table 2.5 Proposed NFPA ratings: degrees of hazard.

| Substance | Health | Flammability | Chemical reactivity | Special hazards |
|---------------------|---|--------------|---------------------|-----------------|
| PMDI | 2 | 1 | 1 | Not classified |
| MDI | 2 | 1 | 1 | Not classified |
| TDI | 3 | 1 | 1 | Not classified |
| Ratings | | | | |
| Health | 2: can cause temporary incapacitation or residual injury under emergency conditions. | | | |
| Health | 3: can cause serious or permanent injury under emergency conditions. | | | |
| Flammability | 1: substance requires considerable preheating under ambient conditions before ignition or combustion can occur. | | | |
| Chemical reactivity | 1: substance is normally stable but can become unstable at elevated temperatures or pressures. | | | |
| Special hazards | relate to reactions under certain circumstances such as unusual reactivity to water, or oxidizing properties. | | | |

If a fire occurs

Small fires involving diisocyanates should be extinguished using dry chemical or carbon dioxide appliances. Water should not be applied unless from a safe distance (e.g. by hoses) and in large quantities. Such fires are usually dealt with by the local trained and equipped personnel.

Large fires involving diisocyanates can be extinguished with large volumes of water, as normally applied from a distance by hoses. Water-based protein or other fire-fighting foams can be effective in extinguishing such fires as well as suppressing the release of diisocyanate vapour: however, there have been cases where the time lost in obtaining such foams has led to more hazardous situations than would have arisen with the immediate use of water.

The local fire services should already have plans of the site showing areas of storage of MDI or TDI, so that they can take preventative action by cooling

these critical storage areas with water to prevent the explosion of metal drums, or the melting and degradation of combustible containers.

As in any fire situation, all nonessential members of the workforce should be moved up-wind of the fire and only trained and well-equipped personnel allowed near to the fire until the fire service takes control of the situation.

Schupp (1999), in collaboration with an industrial fire service, undertook studies which included extinguishing fires of MDI and TDI, using foam based on water and detergent. The studies include details of the decontamination of the fire residues, as well as the analysis of gases from the two pools, before and during the fire.

Actions after a fire incident

Immediate action

The first action is to have the area monitored for diisocyanates in the air. Only after that should personnel be allowed on the site. A decision must be made on how to remove residual MDI or TDI. This may be very difficult if large quantities of material of unknown condition are left. Collaboration with both the diisocyanate manufacturers and fire services may be essential. Small quantities of diisocyanates should be neutralized by the methods given in *Part 2, Key Theme 3*. Fire residues and contaminated extinguishing waters should be tested before disposal, in accordance with local regulations. Testing should be of both chemical and biological aspects of water quality. An example of a test report is that of Cheesman and Girling (1990) which indicates how much the extinguishing water should be diluted to allow fish life to be sustained.

Further action

All aspects of the involvement in the fire of MDI or TDI should be reviewed in detail, to understand what further precautions should be implemented.

On-going action

Whenever there are significant changes to plant processes or to site lay-out the fire safety implications should be reviewed.

Transport of MDI and TDI

MDI and TDI are routinely transported in large quantities by land, by sea and by air. Most is transported without a drop being spilled. This safe transport requires active cooperation between all those involved in the transport and distribution chain. Appropriate handling procedures must be established for the wide variety of container sizes in use. Examples of these include:

- ships' tanks, typically 1 000 000 litres;
- rail tankers/ cargo tank trucks, typically 40 000 to 80 000 litres;
- road tank containers, ISO containers and other transferable tanks, typically 20 000 litres;
- intermediate bulk containers, typically 1 000 litres;

1000 litres is equivalent to
264 US gallons

- cylinders, for example 200 and 870 litres;
- metal and plastic drums, typically 200 litres;
- metal cans, pails and totes of various sizes and designs.

Care must be exercised to avoid all contamination of the chemicals, particularly by moisture, and to maintain specified temperatures. Preservation of product integrity is important both for the manufacture of high quality polyurethanes, and for safe handling. Guidelines to establish appropriate high standards for the distribution of MDI and TDI have been prepared (API, 2000a, 2000b; ISOPA, 2002).

Transport regulations

Examples of transport regulatory authorities and requirements are:

| | | |
|-------------|------|--|
| Air: | ICAO | International Civil Aviation Organization |
| Sea: | IMO | International Maritime Organization |
| Road: | ADR | Accord Européen relatif au transport international des marchandises dangereuses par route |
| Rail: | RID | Règlement international concernant le transport des marchandises dangereuses par chemin de fer |
| Con-tainer: | CSC | International convention for safe containers |

There are United Nations (UN) recommendations, which are presented as *Model regulations on the transport of dangerous goods*, addressed to governments and international organizations, who apply them as a basis for national and international transport regulations. If particular national authorities apply different requirements from those of the international organization, then the more stringent requirements have to be followed. For example, the US Department of Transport requirements are more stringent than the UN recommendations.

The criteria for transport classification are broadly based on acute hazard and physicochemical properties. The UN recommendations classify substances into nine classes as a function of these inherent properties, and regulated substances are given a UN Number. TDI has UN Number 2078; it is classified as Toxic Class 6.1. For the transport of packaged TDI goods, UN Packaging Group II performance standards must be complied with. MDI has been de-classified by the UN, and hence has no UN number. In the United States, a number of regulatory requirements must be met when transporting TDI by any means, and when transporting MDI in quantities greater than 5000 lb.

It is accepted practice for those transporting diisocyanates by road to carry written instructions for an emergency situation. This can take the form of an emergency procedure guide, as given in Figure 2.15. In the United States this includes a shipping paper which must contain an emergency contact telephone number, and a statement that the material is shipped in compliance with the regulations and emergency response information.

In Europe there is a system of TREMCARDS (transport emergency cards) which applies to consignments of dangerous goods transported under the ADR and RID areas of influence. These cards also give information on properties of the chemical, and on the personal protection required in case of spillage, as well as an emergency telephone number to be used in the case of incidents. Although MDI is no longer classified by the UN, it has become accepted practice in Europe for the producers to provide carriers with printed instructions for emergency situations.

| |
|---|
| Contents of a typical Emergency Transport Guide for a diisocyanate |
| Transport classification numbers |
| Name of substance |
| Description of substance (colour, freezing behaviour, water miscibility) |
| Nature of hazard (toxicity, irritancy, fire behaviour) |
| Protective equipment required (respiratory protection, goggles, clothing) |
| In the event of an emergency |
| Whom to notify |
| Actions to take if there is a spillage |
| Actions to take if there is a fire |
| First Aid procedures |

Figure 2.15 Contents of a typical emergency transport guide for a diisocyanate

MDI and TDI: transport temperatures

To maintain product quality and for safety reasons, it is important that MDI and TDI are transported at suitable temperatures. There are several grades of MDI and TDI, and many types of derived prepolymers and other partial reaction products. The supplier's guidance should always be followed on suitable transport temperatures for these products.

Where possible, suppliers deliver diisocyanates at temperatures appropriate for their customers' use. It is common practice for suppliers to charge polymeric MDI and TDI into the tanks used for transport near the top of the recommended temperature range, to allow for some cooling during transport. Deliveries in bulk are often planned so that the customer receives the diisocyanate at the temperature preferred for handling and use. Tanker deliveries of polymeric MDI are typically between 30 and 45 °C (86 and 113 °F). The viscosity of polymeric MDI depends on the temperature and if the temperatures are too low it may be difficult to pump.

The quality of pure MDI will deteriorate quickly unless it is handled correctly. MDI dimer may form and result in turbidity or the precipitation of dimer solids in the liquid. Pure MDI melts at 40 °C (104 °F). Suppliers deliver pure MDI either in the frozen state, or as a liquid held between 40 and 45 °C (104 and 113 °F), to minimize dimer formation. The optimum temperature for storing pure MDI over extended periods is below 0 °C (32 °F).

TDI is delivered in bulk at 20 to 30 °C (68 to 86 °F), and in drums without temperature control. It tends to crystallize out at temperatures below 15 °C (59 °F). If crystallization of 80/20 TDI occurs, it is important that it is well mixed after thawing completely to ensure that the two isomeric forms are distributed homogeneously. The recommended temperature range for handling TDI in the workplace is greater than 15 °C (59 °F) and not above 30 °C (86 °F).

See Part 2, *The workplace* below for more details.

Typical containers for the transport of diisocyanates

Rail tank cars, road tankers and inter-modal tank containers

Tanks and equipment can be constructed of mild steel (coated), but stainless steel is recommended for ease of cleaning and minimizing product deterioration. Rail tank cars (Figure 2.16), road tankers (Figure 2.17) and inter-modal tank containers used for the transport of all chemicals must meet the design and construction requirements of the various national and international regulations. The regulations cover the requirements for aspects such as construction materials, welding, wall thickness, gaskets, valve protection and venting devices and should be consulted for detailed information.

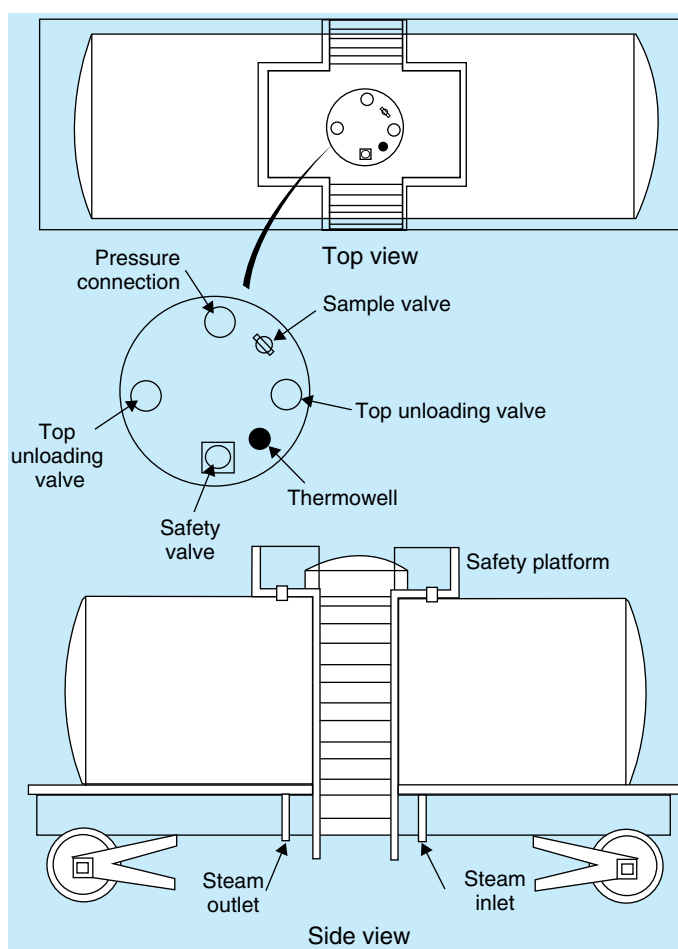


Figure 2.16 Typical tank car

It is recommended that product vapour return and dry gas pressure connections on all tanks/vehicles should be clearly labelled. The labels should be in the language(s) of the consignor and destination and in an international language, often English, on journeys through other countries.

Tanks should be thermally insulated to minimize deleterious temperature deviations. The insulation will provide extra protection in the event of an

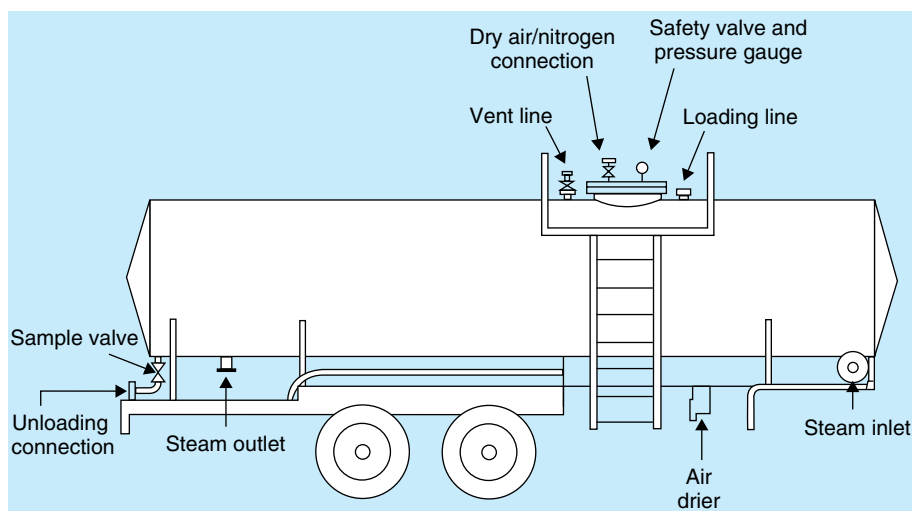


Figure 2.17 Typical tank truck

accident or fire in the vicinity. Heating coils should preferably be oil filled. They should be located on the exterior of the tank, and regulated to a maximum temperature of 60 °C (140 °F).

Although some regulations permit bottom outlets, top outlets through a dip tube may be preferred to prevent the possibility of leakage. Tanks should be fitted with connections for vapour return lines, which are typically 2 inches in the USA, and 50 mm in Europe. Pressure relief valves, protected by bursting discs, should be fitted. A pressure gauge should be fitted in the space between the bursting discs and the relief valve. Vacuum relief valves should be present to prevent negative internal pressure, for example a vacuum that develops during unloading by pump. Fittings must be available for pressurizing the tank car with dry air (dew point –40 °C, which is also –40 °F) or dry nitrogen to assist in unloading or to apply a blanket to prevent entry of moisture.

A rail tank car must have roll-over crash protection on external fittings so that the rail tank car will not leak if involved in an accident. Thermowells for temperature-measuring devices should be fitted and have the appropriate relief devices to prevent spraying of the product in the event of damage to the thermowell. Emergency information panels (placards) should be located on both sides of the tank as well as at both ends, so that if the container is lying on its side following an accident, then at least one label will be visible. Any opening which people are required to enter at any time must exceed a minimum diameter. The cover should have hinged swing bolts.

Intermediate bulk containers

Intermediate bulk containers (IBCs) allow efficient transport and handling of diisocyanates in quantities convenient to many polyurethane manufacturers. The term IBC in Europe refers to a container of size 1000 litres, whereas in the USA the term covers containers of a range of sizes between drums and bulk transport vessels. Some IBCs have casings which allow lifting by a fork lift truck; other IBCs can be moved on pallets. IBCs with metal frames can

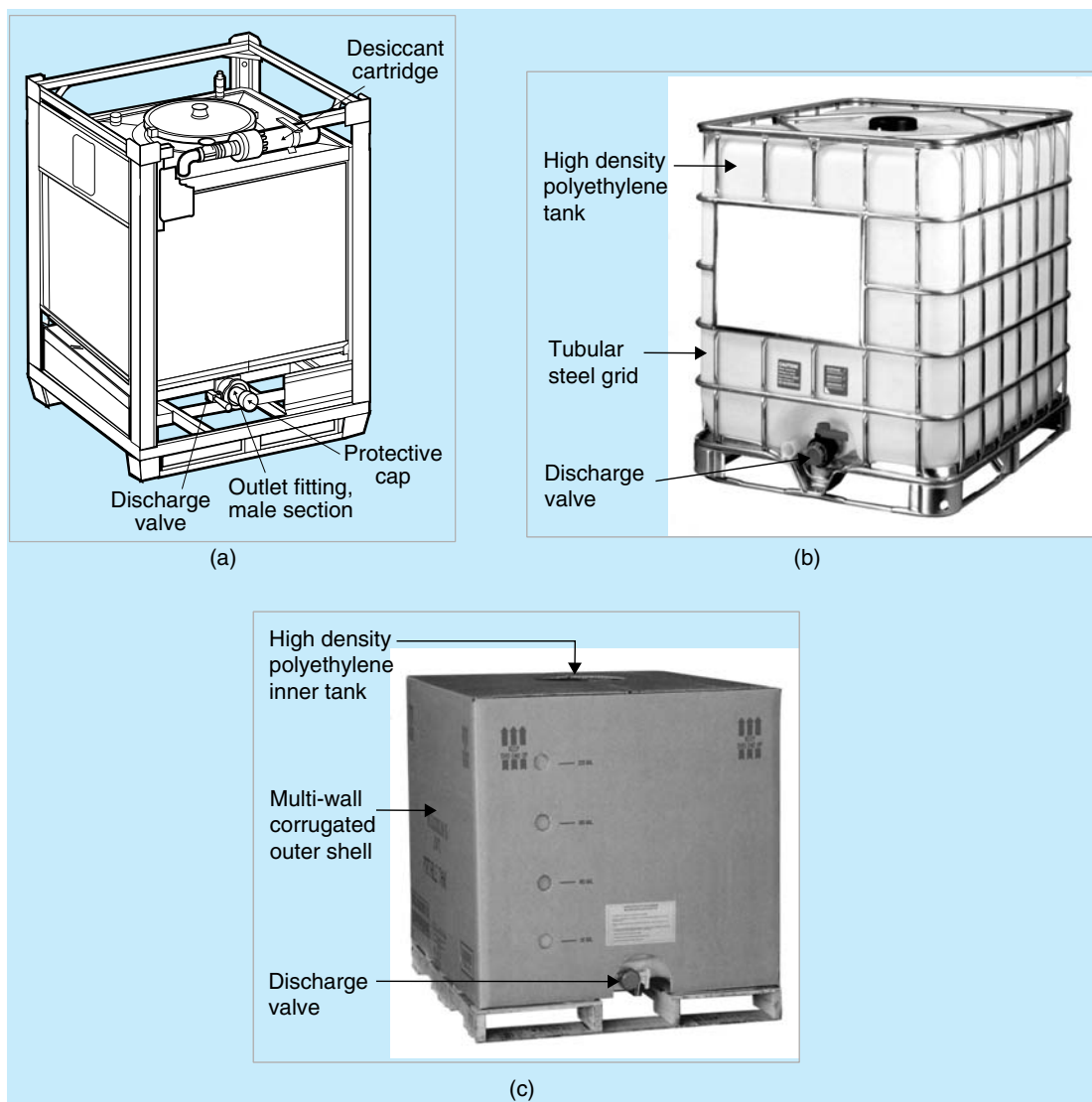


Figure 2.18 Some types of IBC. (a) Stainless steel IBC. Reproduced with permission from *Guidelines for the Design and the Handling of Stainless Steel IBCs for Diisocyanates and Components of Polyurethane Systems*, ISOPA, 1996. (b) IBC with a polyethylene tank within a stainless steel grid (Schütz Container Systems, Inc., 1995). (c) IBC with a polyethylene tank within a multi-wall corrugated shell, Hoover Bulkdrum® II (Hoover Materials Handling Group, Inc., 1996)

also be moved by rolling conveyors, and the containers can be stacked up to three high when filled (Figure 2.18).

IBCs are available in different designs and materials. IBCs suitable for either TDI or for polymeric MDI are made from stainless steel (ISOPA, 1996, 1997b). IBC transport for TDI is restricted to the use of metal IBCs only. Metal and nondisposable polyethylene IBCs are refilled by the supplier. Some IBCs for polymeric MDI consist of a disposable polyethylene container inside an outer casing. These containers are disposed of safely when empty by specialist contractors.

Although MDI is no longer classified by the UN, it is generally agreed within the diisocyanate-producing industry that the packaging should meet the recommendations of UN Packaging Group III. IBCs are not recommended for the transportation of pure MDI because the containers are unheated and the pure MDI would solidify due to its relatively high freezing point, 40 °C (104 °F).

An IBC should not be filled to more than 98 % of its capacity. The container lifetime should be monitored and recorded by means of periodic inspections. Suppliers will be able to advise on the most suitable container for a particular user situation.

Drums

The material of the drum, including any fittings, should not cause product deterioration. International modal regulations include a requirement for the drums to bear a certification mark indicating compliance with the UN packaging performance standards. In some countries regulations may differ from these and must be consulted directly. There should be an inspection regime immediately prior to drum filling. Drums must be undamaged, dry, clean and free of rust or other particulate matter.

Drums should be wire-banded or shrink-wrapped when transported on pallets to prevent movement. Drums of pure MDI should be transported in refrigerated containers at –20 to 0 °C (–4 to 32 °F) to prevent dimerization of the MDI. Diisocyanate drums should not be transported on a truck with flammable materials.

Pallets of drums, shrink-wrapped or banded, can be unloaded by a fork lift truck. Individual drums can be unloaded using a fork lift truck fitted with special drum handling equipment. Drum clamps or grabs are suitable for some designs of drums, but may cause damage to others. The supplier should be consulted if there is any doubt about the type of equipment best suited for a particular design of drum. Where fork lift trucks are not available, drums may have to be unloaded manually. Ideally, the drums should be carefully rolled down an inclined plane. The dropping of drums from a truck should be done only with extreme caution by rolling the drum from the tailboard and dropping it on to a drop cushion, a slab of high density foam or a bed of tyres. During unloading, drums should be inspected for damage and to ensure that they are properly labelled. If damaged drums are identified, they should be examined carefully for splits, leaks or punctures. Leaking drums should be sealed if possible and removed to a dry, well-ventilated area and the contents transferred to other suitable containers. Empty drums should be decontaminated or sent to a specialist contractor. Bulging drums are evidence of pressure build-up and they must be segregated with great caution, and dealt with as described in *Key Theme 6, Dealing with accidents*.

Other containers

Various other containers are also used for the transport of polymeric MDI and of TDI. These include totes of various types and sizes, pails (small drums with top handles) and pressurized carbon steel cylinders, ranging from a drum to a bulk container in capacity. In Japan, small containers such as 18 litre cans

See Part 2, *The workplace: storage and use of MDI and TDI* for further information.

are commonly used. Some types of containers are used by one supplier only, who should be consulted directly if specific questions arise about their use or suitability for particular applications.

Responsibilities of carriers

Safety auditing of drivers and vehicles delivering bulk consignments

Only professional carriers, who understand the safety precautions that must be taken, should undertake transportation of MDI, TDI and modified diisocyanates. Regardless of the mode, i.e. land, rail, air, inland waterway or sea, the carriers should demonstrate through policies, programmes and operating practices that they have management commitment to safety and regulatory compliance. The carriers selected must exhibit their ability to transport all diisocyanate materials in a manner that assures the health and safety of their employees, the end user, the communities through which they travel, as well as the environment. It is important that manufacturers and distributors develop safety review processes which measure the carriers' safety fitness and that feedback is provided to the carriers on any safety performance deficiencies. This process should establish measures and goals that will lead to long-term safety improvements.

Contractual arrangements with carriers should state explicitly that the transport must not be subcontracted without prior written approval of the supplier. Thus, when multi-modal transport is used, the final carrier must not be regarded as the subcontractor; the MDI or TDI supplier should also control that carrier. The primary carrier should not change the secondary carrier without prior written approval of the supplier. Operating procedures at the discharge facility should be the responsibility of the receiver (see below).

Product training for drivers

National and international agreements require that drivers of road tankers (tank trucks) or transport units carrying tanks over a defined capacity must have completed a training course on the particular requirements that have to be met during the transport of dangerous goods. In addition, the hazards associated with MDI and TDI are such that drivers should be specifically trained either by the manufacturers or the carriers to understand the particular nature of the problems which may arise during the transport of these products and the actions to be taken in an emergency.

Therefore, before drivers are allowed to transport MDI and TDI, they should have:

- received training to the standards required by the regulatory authorities in the areas in which they will operate. In the United States, a driver should have a Commercial Drivers License containing a Hazardous Materials endorsement.
- participated successfully in a specific training course for diisocyanates. A training package is available (ISOPA, 2000).

Before a manufacturer enlists a carrier he should ensure that the carrier can document that all drivers transporting MDI and TDI have been trained according

Carrier safety audit protocols have been developed in the USA by the American Plastics Council and in Europe by Conseil Européen des Fédérations de l'Industrie Chimique (CEFIC).

Transportation guidelines
API (2000a, 2000b);
SPI (1996g); ISOPA (1992).

to the regulations. A supplier should include training as an item to be addressed in the carrier audit programme.

Pre-transfer inspection

Written operating instructions covering the loading and unloading operations of MDI or TDI should be available. Information and training regarding the specific hazards of MDI and TDI must be given to all individuals involved in the loading and unloading. Additionally, workers must be trained in the proper procedures for the operation of the loading and unloading equipment in both normal operations and in emergency situations.

Drivers must also be familiar with safety procedures and the use of safety equipment at the loading and unloading points which should include a safety shower and eye wash facilities. Appropriate personal protective equipment must be available for loading and unloading operations and workers must be trained in the correct use of this equipment.

Protective equipment for the transfer of MDI and TDI products

For the transfer of MDI and TDI, personal protective equipment should be used. This will consist of:

- goggles;
- safety helmet;
- overalls (coveralls);
- impervious gloves;
- impervious boots.

For TDI, and where there is a possibility of inhalation of vapour of MDI, for example during sampling or the connection/disconnection of hose joints, suitable respiratory equipment should also be worn.

Self-contained breathing equipment should be provided ready for use at the tanker discharge points for use in case of a spillage or other emergency. Persons dealing with a spillage of TDI, or of MDI at elevated temperatures, should be protected by impervious suits and *must* use respiratory protection in addition to the normal protective clothing described above (Figure 2.19).

See Key Theme 4: Using personal protective equipment.

Distribution of MDI and TDI

Road transport

The carrier is responsible for the safe transport of MDI and TDI by road from the loading point to the unloading point and should plan a route that can be given, on request, to the supplier. Compliance with bridge, tunnel or local routing regulations or restrictions is entirely the responsibility of the carrier. As is usual with all chemicals, the route should follow major roads and avoid areas of high population density where possible.

Temperature checks of the tank contents should be made regularly and logged. If the temperature of the tank contents should rise more than 5 °C (10 °F) above that specified by the supplier, the driver should immediately

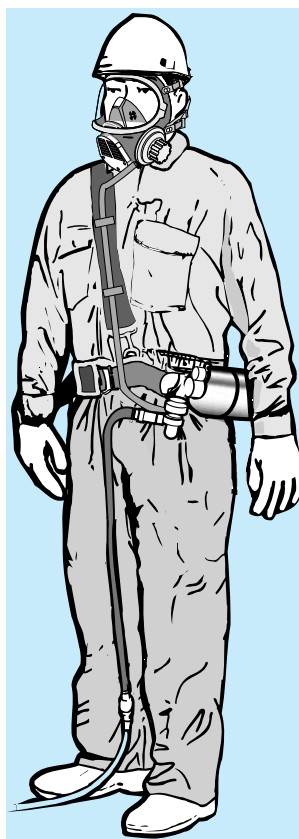


Figure 2.19 Full protective equipment

telephone the supplier to seek instructions. Drivers should make checks during the course of transportation as follows:

- when there is a change of driver;
- after the vehicle has been driven for 3 to 4 h, or after the vehicle has been driven for 240 km (150 miles), whichever occurs first.

Safe parking is essential. Drivers of vehicles transporting MDI and TDI must ensure that the vehicle is either supervised at all times or is parked in a safe place. A secure depot or secure factory premises should be used whenever possible. Preferably, parking should be in an isolated position in the open in an area that is lit at night. It is strongly recommended that receivers provide secure parking for vehicles that have arrived outside specific access times.

When severe weather conditions are experienced during the transport of MDI and TDI the vehicle must stop at the next suitable parking place. The vehicle should not continue with the delivery until the weather conditions improve. All delays during transport, whether caused by severe weather conditions, breakdown or any other reason, must be reported to the customer and/or supplier as soon as possible.

In the event of an accident during the journey involving the immobilization of the vehicle, product spillage, or a threatened loss of containment, the

procedure for obtaining emergency assistance as specified in the emergency guidance procedures laid down by the suppliers should be followed. Details of the accident must be reported to the supplier and/or customer urgently.

Rail transport

The appropriate railway company or authority is responsible for the safe transport of the MDI and TDI by rail from the dispatch siding to the final reception siding. The selection of the route, intermediate stopping locations and cessation of traffic due to severe weather conditions are matters to be decided by the railway authorities, and should be reported to the supplier.

The railway companies will intervene in the event of an emergency involving a rail car containing MDI or TDI. These companies should already have been made aware of product hazard information to aid railway hazardous cargo intervention teams. It is recommended that rail tank cars should be labelled with the supplier's telephone number for use in an emergency. Railway companies should also be made aware of any available transport emergency scheme for providing assistance at transport incidents.

Where road–rail–road movements are arranged which are not driver-accompanied during the rail stage, particular attention must be given to ensuring that the road vehicle performing the final delivery is accompanied by the appropriate emergency response information.

Transport by sea or inland water

MDI and TDI can be transported in:

- bulk ocean tankers or inland waterway vessels;
- inter-modal tank containers that are lifted on and off container vessels;
- inter-modal tank containers, with roll-on/roll-off chassis;
- intermediate bulk containers (IBCs) which should be transported in freight containers;
- nonbulk packaging such as drums.

All relevant local, national, federal and international regulations such as the International Maritime Dangerous Goods Code must be observed.

Because of the nature of the activity, a number of different organizations may be involved in the operation of transporting MDI and TDI from supplier to customer. These may include the shipping company, port or harbour authorities and carriers. The supplier should consider carrying out a safety audit of the following transport operations:

- the loading/unloading facilities at container terminals;
- emergency handling within hazardous cargo yards at container terminals.

Unloading operations

Criteria for unloading facilities

It is important that unloading facilities are correctly designed and constructed. There should be an unrestricted escape route from the unloading site. The operation of unloading MDI or TDI from any road tanker, tank container, rail

tank car or small tank container is potentially hazardous. Both pressure or pump methods are used. There are differing views on the relative safety of the two methods. If pressure unloading is used, the displaced vapour cannot be returned to the tanker, and has to be removed from the air before venting to the atmosphere. If pump unloading is used, the vapour will be returned to the tanker and the potential releases to atmosphere will be negligible (there is still some venting via a scrubber or filter at the end of the operation). The equipment should be subject to regular reviews or audits to ensure the maintenance of the required standards.

Criteria for hoses

It is strongly recommended that all hoses used for product unloading be dedicated to MDI or TDI service and either be fitted with a ball valve at the tanker connection end or have an equivalent means of sealing the hose. The unloading hoses for diisocyanates should preferably have different couplings (size and type) to prevent inadvertent connection to the wrong storage vessels. Colour coded hoses stamped 'For diisocyanate use only' are useful additional safety measures. Pressure testing is recommended prior to initial use, and quarterly thereafter.

Operating procedures

Written operating procedures covering all aspects of the unloading of MDI and TDI must be prepared by the owner of the unloading facility and agreed with the carrier, with the division of responsibilities clearly defined and followed. However, before the product is unloaded, the receiver should carry out checks to verify that the product complies with the documentation, and then certify in writing that:

- the goods can be safely received at the storage location;
- the hose is connected to the correct point.

The lines should be installed to the customer facility first, and the diisocyanate tank second. Connection and disconnection of the product lines should be carried out with great care, to prevent contamination of the diisocyanate. At least one person, driver or operator, should be present and watch the discharge all the time (API, 2000a, 2000b). Nonessential personnel should leave the area during discharge. Exclusion barriers should be provided to ensure that nonessential personnel do not enter the area inadvertently during unloading. Product transfer can be monitored by means of flow meters or by loss in weight of the tank cars.

Protective equipment for operators

All necessary protective clothing and emergency equipment should be available for unloading operations. Persons should be trained in the correct use of this clothing and equipment. Whenever the driver leaves his vehicle during unloading, he should take with him his personal protective equipment to be sure of its availability in the event of an emergency.

See Part 2, *The workplace: storage and use of MDI and TDI* for further details.

Inspection of the bulk storage facilities

The conditions for the storage of bulk deliveries of MDI and TDI at a customer's premises are the customer's responsibility. It is recommended that suppliers, in cooperation with customers, should arrange an inspection of the bulk reception facilities prior to an initial delivery and at agreed intervals. The objective is to ensure that good safety standards pertain during product handling and storage. The site for the location of storage vessels should be carefully chosen. It is particularly important that the discharge site be constructed so that any spillage is contained and is not able to enter surface water or drainage systems.

Check list of equipment guidelines and requirements for tank truck deliveries

Manufacturers of MDI and TDI may provide their customers with a check list relevant to their particular situation to ensure that the most important safety requirements during unloading of the diisocyanates are considered. The following is an example.

EQUIPMENT GUIDELINES AND REQUIREMENTS FOR TANK TRUCK DELIVERIES

Tank truck unloading area

-
- ✓ Suitable location of unloading site
 - ✓ Safe access/egress for tractor, trailer, driver and unloading operator
 - Impervious spill containment
 - Unimpeded access to a safety shower and eyewash
 - Fire extinguisher (as per specific MSDS)
 - ✓ Wheel chocks utilized
 - Communications access (radio, telephone)
 - ✓ Access to spill cleanup materials (as per specific MSDS)
 - ✓ Written unloading procedures
 - ✓ Trained personnel—product, equipment, process and procedures
 - ✓ DOT training requirement met (49 CFR 172.700–704)
 - ✓ Appropriate personal protective equipment utilized (as per specific MSDS)
 - ✓ All fittings, piping, valves and tanks clearly identified
 - ✓ Vapor return or proper treatment of vapors from storage tank
 - ✓ Piping material of construction to be carbon steel or stainless steel
 - Flanged, welded pipe connections
 - ✓ Piping traced, insulated and jacketed as necessary for temperature control
 - Male Kamlok® type fitting on customer piping for unloading hose connection
 - ✓ Isolation valve as close as possible to unloading hose connection
 - Check valve on storage tank side of unloading hose connection
 - Drain/vent valve between isolation valve and unloading hose connection
 - ✓ Fittings and drain valves capped or plugged when not in use
 - Carrier-supplied hoses utilized for product transfer and vapor return

- 2 inch piping and hoses for isocyanates
 - 2 inch hose and fittings for vapor return
 - $1\frac{1}{2}$ inch diameter piping minimum for vapour return
 - Isolation valve as close as possible to vapour hose connection
-

Pump unloading

- ✓ Customer-supplied unloading pump
 - Sealless pump
 - Pumps, strainers and filters inside secondary containment
 - Strainer on suction side of pump
 - ✓ Piping system and equipment drain valves to be capped or plugged when not in use
 - Pressure gauge on discharge side of pump and on suction/discharge sides of filters
 - Bypass around unloading pump (may require proper treatment of vapours)
 - ✓ Vapour return to tank truck or proper treatment of vapours from storage tank
 - Pressure vacuum combination gauge on vapour return piping
-

Pressure unloading

- ✓ Nitrogen or dry air source with -40°F dew point
 - Pressure gauge on unloading piping
 - ✓ Proper treatment of vapours from storage tank
-

✓ Supplier requirement • Best industry practice

This information is taken, with permission, from the 2001 product stewardship literature of Bayer Corporation, USA.

Accidents and emergencies

Emergency procedures

All persons dealing with emergencies involving MDI or TDI should wear full emergency equipment; the use of self-contained breathing apparatus is essential. See *Key Theme 4: Using personal protective equipment*. If a diisocyanate leak or spill occurs during transport, the diisocyanate should be contained as much as possible by the use of wet earth or wet sand where local conditions allow it. See *Key Theme 6: Dealing with accidents*. In all cases of large spills or leaks the supplier of the diisocyanate should be contacted without delay for advice and help relevant to the specific situation. Small spills or leaks should be treated with an absorbent material and neutralized and the residues disposed of safely in accordance with local regulations. See *Key Theme 3: Neutralization, decontamination and disposal of wastes*.

MDI and TDI do not ignite easily, but in a fire will burn and give off combustion gases typical of any organic material containing nitrogen. See *Part 5.5. Fire behaviour of MDI and TDI*.

Schemes for providing assistance at transport/unloading emergencies

National emergency response schemes exist in various countries throughout the world. All responsible chemical companies involved in the transport of MDI and TDI should ensure that there is a means of receiving transport emergency messages (24 h manning) and for providing expert advice to minimize any hazard arising from an incident on road, rail or water. Additionally, they may attend the scene of the incident, or may 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 would be:

- to offer advice based on technical product knowledge;
- when requested by and agreed with the emergency authorities, to organize the provision of spare vehicles/pumps/hoses/other equipment, cargo transfer and decontamination;
- to be prepared on behalf of the emergency authorities to employ their technical expertise in the conduct and supervision of remedial action to render the incident safe.

Because of the large geographical areas involved in the transport of MDI and TDI, the ability of an individual chemical company to provide expert advice quickly at the scene of an incident may be severely restricted due to the distance involved. However, a contact point for technical information should always be available.

The workplace: storage and use of MDI and TDI

Additional information will be found in the preceding *Key Themes*.

MDI and TDI are very widely used in many locations for manufacturing polyurethanes. These range from small operations with a few drums of diisocyanate stock to very large production units with fully automated systems, and bulk storage in tank farms. However, there are common approaches to protecting the workforce, and common requirements for preserving product integrity that may have a bearing on safety. There are also requirements to minimize releases and to dispose of waste materials safely, so that local communities and the environment are not adversely affected.

Once MDI or TDI has been accepted into storage (see *Part 2, Transport of MDI and TDI*) the responsibility for its safe handling and use rests with the site management. Supervisors need to ensure that the responsibilities for safety are well defined, understood and adhered to. Provision of suitable training and retraining on all aspects of the safe handling of MDI and TDI form an important part of ensuring that safe working practices are applied, whether during normal operations or in the case of emergencies. Routine medical surveillance for those potentially exposed to diisocyanates should be provided. Visitors to all chemical sites need special consideration, as they may be unaware of the necessary precautions where diisocyanates are being handled.

See *Key Theme 2: Protecting health*.

Designing the systems and minimizing the risks

An integrated approach to workplace risk management has to start with the recognition that there will be no single solution for all situations. Each type of process, automated or manual, and each storage facility will require its own control systems, maintenance schedules and training procedures. Care must be taken to ensure that these comply with regulations and local practices. The engineering control of MDI and TDI exposure will generally fall into two categories: physical barriers to minimize releases of diisocyanate into the workplace and exhaust ventilation. Whilst control measures by engineering means are always preferred to personal protection, the normal personal protective equipment for chemical environments will always be required.

The first step in designing the systems and minimizing the risks is to assess the ways in which people can be exposed to the materials used. Since releases can be airborne (vapour, spray, aerosols or dust), solid or liquid, exposure can be either by inhalation or by skin contact. It is difficult to predict which control strategies will be required for a particular process without actually measuring the releases from that process under normal working conditions. In general, the inhalation risks are greatest where the process involves spraying, or heating in the absence of adequate ventilation. Particular problems may arise during maintenance when work may need to be carried out in confined and unventilated spaces.

MDI and modified MDIs are of very low volatility, and present very little vapour risk unless heated or sprayed, though solid MDI in the form of flake can present a risk if the dust is inhaled. MDI may be released from rising foam, especially near filling holes or air vents in large closed moulds. Although the concentrations may be low and of brief duration, the need for ventilation at these points may need to be considered. Aerosols are produced during bonding processes which use sprayed MDI adhesives or during spray foam insulation work. Air-supplied respiratory protection is essential for manual dispensing or spraying of MDI-based foams and adhesives, unless measurements demonstrate that engineering control is sufficient to reduce the concentration of MDI to below the Occupational Exposure Limit (OEL). Manual dispensing of one-component foam does not normally require such protection. Spraying of reaction mixtures outdoors always requires air-supplied respiratory protection since engineering control is not possible.

TDI is much more volatile than MDI. Exhaust ventilation is usually essential in the processing of TDI-based polyurethanes, whereas it may not always be needed for the processing of MDI. It should be recognized that there are other chemicals used in the manufacture of polyurethanes and these may also present hazards associated with toxicity or environmental impact. These need to be investigated in their own right.

Processing equipment should be designed with the demands of the user in mind, to make it simple to use, clean and maintain. Whenever possible, control of releases into the workplace should be part of the design, especially as there is increasing pressure to minimize releases and waste, and as the costs of the treatment of releases and waste disposal rise ever higher. Improvement in the design of existing plant is often economically justifiable when compared to the costs of bolt-on remediation or down-stream charges for waste handling.

A process that requires the operator to wear respiratory protective equipment and impermeable clothing continuously as a necessary precaution is to be avoided. Personal protective equipment will, however, still be needed for various reasons discussed below. Careful examination of a block diagram of the plant or process can yield foreseeable points of releases. A critical analysis of these areas will provide solutions to eliminate or minimize the release.

Assessment of workplace exposure

Every safety scheme will need to incorporate an assessment of the potential exposure of the workforce. This assessment is central to risk management. The materials processed and the process equipment all need to be included in the assessment. The different jobs in the workplace where diisocyanate exposure may possibly occur, including maintenance, repair and cleaning tasks, must also be assessed. The assessment may well be rather complex; its conclusions will then need to be simplified into action plans and instructions. The assessment will be iterative. A quick review may reduce the safety options from many to a few. A more detailed review leaves two or three preferred options. Each then needs a thorough design costing and review before a final choice of control measures is made. The assessment may conclude that different levels of personal protection are required for different jobs.

Raw materials

Even before chemicals are delivered, the supplier should provide comprehensive safety information about them such as product data sheets. Most manufacturers of MDI and TDI subscribe to schemes of Product Stewardship under which they commit to provide information and advice on their products. When products are purchased from merchants or secondary suppliers, and not direct from primary manufacturers, the information may be less complete. Even when labels, or documents such as material safety data sheets giving all the basic information, are made available there may be unresolved questions on safety. Those handling diisocyanates should make every effort to obtain help from their suppliers to resolve safety problems.

Engineering control considerations

In many countries, legislation is moving away from specific items on a checklist towards compliance with principles. The extent of this change varies from country to country. In the European Union, for example, quite general essential health and safety requirements are set down, applicable to all types of machinery and processes.

When new machinery is to be purchased, the following points should be discussed with the suppliers of the machine and of the chemicals that are to be used:

- equipment scope and limitations;
- materials consumed and produced;
- types of potential releases;
- extent and location of possible releases;
- control measures needed;

- constraints on implementation of preferred control measures;
- training, maintenance and supervision needed;
- running and waste disposal cost implications of the process.

Many of the points above are equally relevant to assessments of existing machinery.

The quality of safety information provided with plant and equipment varies greatly. For example, the European Union requirements apply only to new machinery. If the process machinery is put together by the purchaser from nonspecific components (drives, valves, etc.) and from local fabrications, there will be little or no health risk control information available from component suppliers and the safety assessment process is then essential.

Strategy for monitoring workplace releases

Stringent workplace exposure limits for diisocyanates have been set world-wide. Moreover, in many countries MDI and TDI have been categorized among substances for which the exposure should be reduced as far below the occupational exposure limit as is reasonable: consequently, measurement of workplace exposure levels will always be necessary as part of a baseline assessment. All possible sources of releases should be dealt with, even if personal exposures are already below the limit.

Monitoring of workplace exposure provides data to:

- verify compliance with regulatory exposure limits.
- estimate exposures of individuals to diisocyanates. Such estimates can be associated with health measurements (see *Key Theme 2*).
- assist in checking the effectiveness of the engineering control measures. This exercise should be accompanied by tests on equipment and factory systems, and logged, so that causes of high exposure can be determined.
- confirm or extend the assessment of the workplace and direct attention to sources of releases that may have been overlooked. It is necessary to consider any anomalies in the results of monitoring, and to look for trends and associations, not merely to record the data as being above or below the limit.

The design of a monitoring strategy will be influenced by the types of engineering control, the polyurethane manufacturing process whether continuous or discontinuous, the diisocyanate, and the range of jobs. A person whose job is exclusively in a workplace containing a well-enclosed, well-ventilated process will be able to rely on the principle ‘if it isn’t getting out of the process, it isn’t getting to me’; and personal monitoring can be reduced in scale and frequency in favour of continuous monitoring close to possible points of emission from the process. However, a person such as a maintenance operator, whose job involves variable work in less predictable conditions, will need better assessment of all the tasks undertaken and may need to wear a personal monitor whilst this is being carried out.

Long-term exposure monitoring results may be presented as an average (8 h time-weighted average) and/or detailed continuous record, depending upon the equipment. An average value may mask exposure peaks which are so high that

they might have a significant effect on respiratory health: this might happen even though the average conforms to the required long-term limit. Averages alone should be used only when there is considerable confidence that there are no high excursions. Personal exposure records need to be linked to the workplace assessment and the results from relevant fixed monitors capable of disclosing excursions.

To develop a monitoring strategy, various stages of data gathering and information collating must be carried out. Initially, an intensive basic survey provides quantitative information on the exposure profile of each worker. This should include those routinely in the workplace, as well as people who are occasionally or intermittently exposed such as cleaners and maintenance personnel. The data are acquired using personal and area monitors covering all periods of significant exposure. There needs to be careful selection of both the sampling techniques and the analytical methods to ensure that they are suitable for the expected emissions. Process activities and any change in circumstances during the sampling period should be logged. Figure 2.20 shows a typical personal monitoring unit being worn by a worker.



Figure 2.20 Worker wearing a personal monitoring unit (figure reproduced by courtesy of Huntsman Polyurethanes)

A second and more detailed survey should be carried out if the intensive basic survey reveals exposure levels above, or close to, the limits. This may involve more detailed personal sampling (over shorter time periods) to identify high excursions and, more commonly, a greater use of area samplers to pinpoint the problem sources. Sampling may be needed from several operations in each work area and for each shift to ensure that representative data are available. On

some occasions there may need to be measurements that distinguish between the activities of individual employees, nominally doing the same job, since work practices may be the source of over-exposure. Once the conclusions have been drawn from the basic and/or detailed survey, and remedial changes have also been tested, the monitoring regime can revert to a routine programme.

Monitoring of a particular job exposure should be repeated monthly, or even more frequently. This should continue until two consecutive determinations, at least 1 week apart, indicate that the exposure no longer approaches or exceeds the recommended occupational exposure limits. Suitable equipment for monitoring workplace exposure is described in *Part 5.7, Sampling and analysis*.

The nature and frequency of routine monitoring depends on the nature of the activity, as discussed above, and should be associated with a record of engineering controls and operating circumstances at the time. For routine operations with well-controlled processes, personal monitoring may be infrequent (e.g. annually), provided that it is combined with audible or visual alarms linked to area monitors. For nonroutine or occasional operations, personal monitoring should be frequent enough to reveal variations, and should be combined with retraining and supervision of procedures when required. Monitoring and other pertinent records should be kept for at least 40 years after the employee's last occupational exposure to diisocyanates, or as required by local regulations (NIOSH, 1978; HSE, 1997b).

Further basic or detailed surveys are indicated (unless a good exposure assessment concludes they are not needed) when

- a new process is started up;
- there has been a significant change of equipment or materials in an existing process;
- there has been a change in the occupational exposure limit;
- there has been a substantial change in the rate, scale, staffing or procedures of an existing activity;
- abnormal, infrequent or special activities are to be carried out (for example, decommissioning, major overhaul);
- there are symptoms (for example, running nose or wheezing) suggesting that there is some unidentified exposure among the workers.

In practice, there are differences between individuals and between shifts giving some *random* variation of monitoring results. However, the results should be checked regularly for *systematic* variation which could indicate the following:

- an individual's poor working practices;
- noncompliance with standard procedures;
- poor supervision;
- significant work load fluctuations.

Such findings should be translated into remedial actions, such as retraining or better management control. In order to get the best value out of monitoring, it needs to be systematic and should include all stages of activities and times of a working day over a period of time. The discovery of high exposures or significant rising trends should result in an investigation and remedial

action. Depending upon the seriousness of the findings important questions might include:

- Is immediate action needed to reduce exposure (for example better personal protection as a short-term measure)?
- Is action needed to control the source of the releases (for example by stopping the process)?
- Is a programme of planned improvements appropriate?
- Is the cause unclear, so that more investigation and a detailed survey are needed?
- Should routine monitoring be intensified or extended?

Tables 2.6 and 2.7 give an indication of typical exposure levels to MDI and to TDI. The data in these tables summarize industrial hygiene information collected over many operational sites over several years. The concentrations found depend upon the actual operational conditions at the time the observations were made, but indicate that broadly accepted occupational exposure limits were complied with (see *Key Theme 1: Know your product*). **However, such figures cannot be used to predict concentrations in other workplaces. Detailed measurements will always need to be carried out.** Table 2.6 summarizes data collected from a wide range of applications and processes within Europe over the period 1993 to 1998 (Dobbs, 1998, personal communication). Various standard sampling methods were used to capture total inhalable MDI (vapour and aerosol). Both personal and fixed position (area) monitors were used. Table 2.7 summarizes data obtained during a comprehensive survey of the UK flexible foam industry over the period 1979 to 1986 (Clark *et al.*, 1998; Bugler, 1999, personal communication). All TDI measurements were made using continuous paper tape monitors worn on the chests of workers during their normal work shifts.

Table 2.6 Typical workplace concentrations of MDI.

| Application | Sampling | Number of samples | Concentration of MDI mg/m ³ |
|---|-------------------|-------------------|--|
| Lamination of rigid foam | Area | 89 | <0.0019 |
| Insulation of refrigerators, freezers and boilers | Area and personal | 50 | 0.0001 to 0.005 |
| Spraying roofing insulation | Area and personal | 15 | >0.05 |
| In situ packaging foam | Personal | 34 | <0.01 to 0.041 |
| Spraying waterproof primer coating | Area | 46 | 0.0001 to 0.008 |
| Oriented strand board: MDI used as binder | Personal | 48 | <0.0001 to 0.021 |
| Particle board: MDI used as binder | Area | 140 | 0.0001 to 0.05 |
| Thermoplastic elastomers: sprayed MDI | Personal | 50 | <0.0001 to 0.0083 |

Typical values for occupational exposure limits are: Short-term (15 min): MDI 0.2 mg/m³. Long-term (8 h): MDI 0.05 mg/m³.

Table 2.7 Typical workplace concentrations of TDI in the UK flexible foam industry.

| Activity | Number of personal samples taken | Number of factories surveyed | Concentration of TDI (8 h time-weighted average) mg/m ³ |
|--|----------------------------------|------------------------------|--|
| Moulding | | | |
| Hot cure: at pouring head | 98 | 4 | 0.007 to 0.028 |
| Hot cure: demoulding, and waxing of moulds | 75 | 4 | 0.005 to 0.006 |
| Cold cure: pouring, demoulding, etc. Some formulations were based on MDI + TDI | 113 | 6 | <0.004 to 0.015 |
| Cold cure: demoulding only | 80 | 5 | 0.006 to 0.0086 |
| Block foam manufacture | | | |
| At dispensing head | 141 | 9 | 0.008 to 0.019 |
| At paper take-off. Respiratory protection often worn | 198 ^a | 9 | 0.017 to 0.047 |
| Moving hot blocks | 282 | 8 | 0.0065 to 0.025 |

^aPredominantly area samples. Workers at paper take-off usually wore respiratory protection.

Typical values for occupational exposure limits are: Short-term (15 min): TDI 0.14 mg/m³. Long-term (8 h): TDI 0.036 mg/m³.

Physical and chemical properties relating to storage and processing

The physical and chemical properties of MDI and TDI impose constraints on the conditions under which they are stored and used in the workplace. Some relevant information is given in *Key Theme 1: Know your product* and further details are given in *Parts 5, 5.3 and 5.4*. Failure to handle and store MDI and TDI under suitable conditions may give rise to risk and be costly. It is essential that MDI and TDI do not become contaminated prior to use. Scrupulous cleanliness of systems is essential for safe and economically viable operations. It is important that even waste diisocyanates are not mixed with certain contaminants, as this can lead to the development of pressure in closed containers and lines. Overheating may cause the formation of hard deposits which could block pumps and lines, with significant losses of the final polyurethane product.

Water either as liquid or as vapour must be rigorously excluded from all products containing free MDI or TDI. The isocyanate groups react with water giving insoluble polyureas with the liberation of carbon dioxide gas. This reaction is slow at workplace temperatures and in the absence of catalysts, but can be vigorous at elevated temperatures. Polyurea formation may cause a build up or blockage especially in vents, valves or mixing heads. In closed containers or in restricted lines contamination by water as liquid may produce carbon dioxide in sufficient quantities to cause rupture. Closed drums can rupture with sufficient force to project them considerable distances. Any evidence of carbon dioxide build up, such as a bulging drum, should be treated

as a potentially serious accident requiring immediate remedial action (see *Key Theme 6: Dealing with accidents* for information on dealing with these occurrences).

Even small amounts of water can cause major problems. When reacted with diisocyanate, 30 ml (about 1 fl oz) of water can release as much as 40 litres (1.5 ft³) of carbon dioxide at normal temperature and pressure. In a 208 litre (55 gal) drum, 95 % full, this could result in a pressure of 2 to 3 bar (approximately 30 to 40 psi), which would probably cause the drum to rupture.

MDI and TDI also react with many common materials, such as alcohols, ammonia, and acids, sometimes with great vigour and with the liberation of heat. Strong bases such as sodium or potassium hydroxides catalyse the rapid dimerization or trimerization reactions producing solid deposits,

possibly with the liberation of carbon dioxide, both of which are undesirable. Further information is given in *Part 5.3, Chemical reactions of MDI and TDI*. Industrial cleaning agents containing sodium or potassium hydroxide must never be used for cleaning lines or vessels. Copper, zinc or their alloys such as brass or bronze, which may be used in pipework or plant fittings, can form reaction products that may lead to product deterioration. Fittings and pipework are now often coated with PTFE to minimize contamination problems. Further advice should be obtained from the equipment manufacturers.

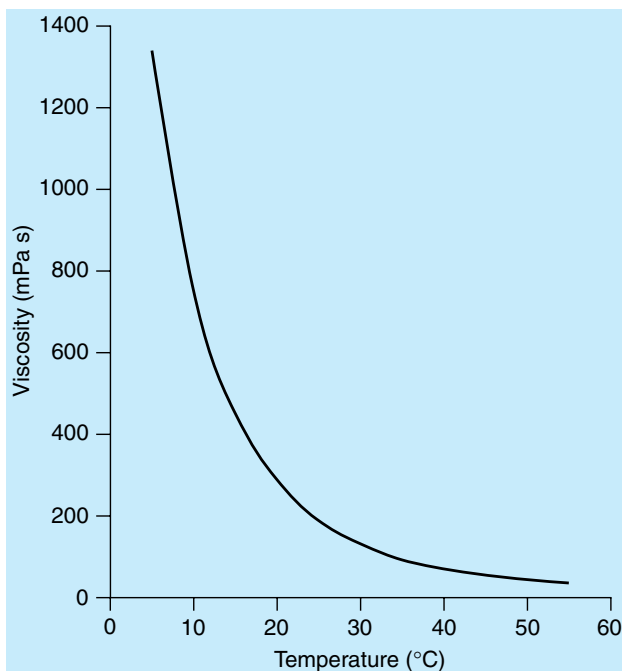


Figure 2.21 Polymeric MDI: temperature–viscosity profile

Figures 2.21 and 2.22 illustrate the changes in viscosity of polymeric MDI and TDI with temperature. Polymeric MDI becomes increasingly viscous with decreasing temperatures and may become difficult to pump. Pure MDI melts at 40 °C (104 °F) and is therefore a solid at normal workplace temperatures.

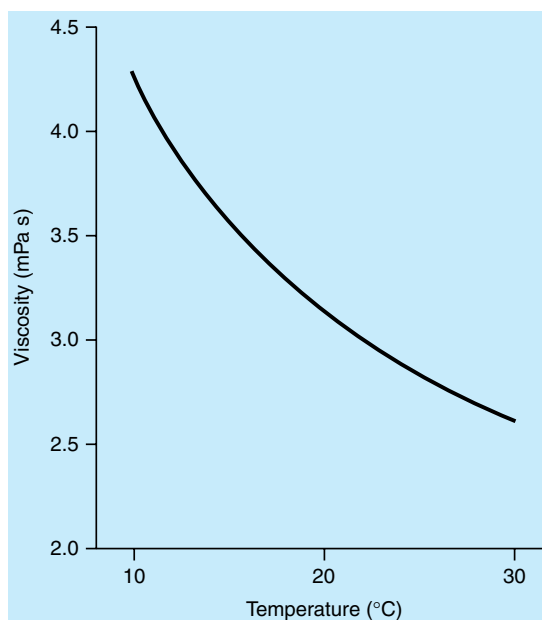


Figure 2.22 80/20 TDI: temperature–viscosity profile

Storage of MDI and TDI

Deliveries of MDI or TDI to a customer will be either as bulk delivery in road tank containers, in rail tankers, in ships' tanks, in various types of bulk containers of intermediate size, or in metal drums, pails or cans of various sizes. Ideally, the bulk storage facilities, which should be sited close to, but separated from, the polyurethane user plants, must be capable of maintaining product integrity and have suitable provisions for the control of accidental releases. Whilst neither MDI nor TDI are easily ignited, both diisocyanates should be stored separately from combustible materials so that they will be protected in the event of a fire.

In some countries there are regulations covering the storage of MDI and TDI in quantities above defined limits. As these may vary from time to time, companies must check those that apply to a particular storage facility.

Relevant regulations

The European Council Directive on the control of major accident hazards involving dangerous substances and preparations applies to the presence on a site of 10 tonnes or more of TDI. The Directive requires safety plans and reports, and consideration of environmental impact. The Directive does not cover MDI.

The USEPA Risk Management Program, the purpose of which is to prevent accidental releases of toxic, flammable or explosive substances, covers the storage of TDI, but not MDI. The Emergency Planning Community Right to Know Act (EPCRA) legislation, which varies by state, requires an inventory of all materials stored on site in excess of defined amounts to be made available to the local emergency planning committee and to the community.

The relevant material safety data sheets should be available prior to the first delivery. The first step in accepting any delivery of diisocyanate into storage must be to confirm that the material delivered is that expected, by ensuring that it is properly labelled and identified. The personnel involved in transferring the material to storage should be wearing the correct personal protective equipment and should be trained in the operations to be carried out. A ready-for-action, self-contained breathing apparatus should be provided

at bulk delivery points for use in case of spillage or other emergency when either MDI or TDI is being discharged. Persons dealing with a spillage of MDI or TDI should also be protected by impervious suits. Appropriate decontamination and other equipment should be readily available to deal with any spillage. Access to an emergency shower and eye wash equipment is also essential. When tank truck deliveries are being made, the driver needs to be told the location of the emergency equipment, which should be tested before unloading starts.

Storage in bulk

Users of large quantities of MDI and TDI will probably have the diisocyanates delivered in bulk in a road tanker, a demountable tank, a rail tank car or by ship tank (see *Part 2, Transport of MDI and TDI*). Diisocyanate supplied in this way will be transferred to dedicated bulk storage vessels. It is good industry practice that the storage vessels should be:

- reached by good roads, allowing easy access to delivery vehicles;
- as close as possible to the using plant;
- sited on stable ground;
- sited away from any fire hazard;
- sited separately from polyol tanks;
- within a bunded (diked) area that will contain the contents if there is a major leak. The containment area should, as a minimum, be able to contain at least 110 % of the total contents of the largest tank within the confinement area. The area should have an impervious surface. Concrete coated with an impervious material should be used; asphalt is not suitable, as it is often porous and the diisocyanate may soften the material. The system should be designed so that any leakage will be contained within the area, and will not enter the surface water or sewage drainage systems. Local regulations may determine the construction details of the containment facility.

Installations are usually designed to meet the particular requirements of a customer. The detailed designs and choices of gauges, pumps, pipes and relief valves require specialist knowledge and experience. The diisocyanate suppliers should be consulted for further details. Figure 2.23 illustrates a layout for a typical diisocyanate storage area.

There should be access to certified tank scales at the site or at another suitable location. Storage vessels should have a minimum capacity to accept the total contents of the delivery vehicle. This will reduce the potential for problems arising from multiple connections. The tanks should be above ground and should be constructed of steel of a grade and type, lined or unlined, which is suitable for the product application. Carbon steel is often suitable for polymeric MDI and for TDI. Stainless steel is preferred for applications where colour variation in the final product must be avoided. The tanks should have certification to allow them to accept positive pressure during pressure unloading or in the event of accidental product contamination. It is better if storage tanks can be located indoors, but if they have to be sited outside and exposed to extremes of temperature they should be insulated. Tank heating jackets or exterior mounted coils may be used for heating where necessary,

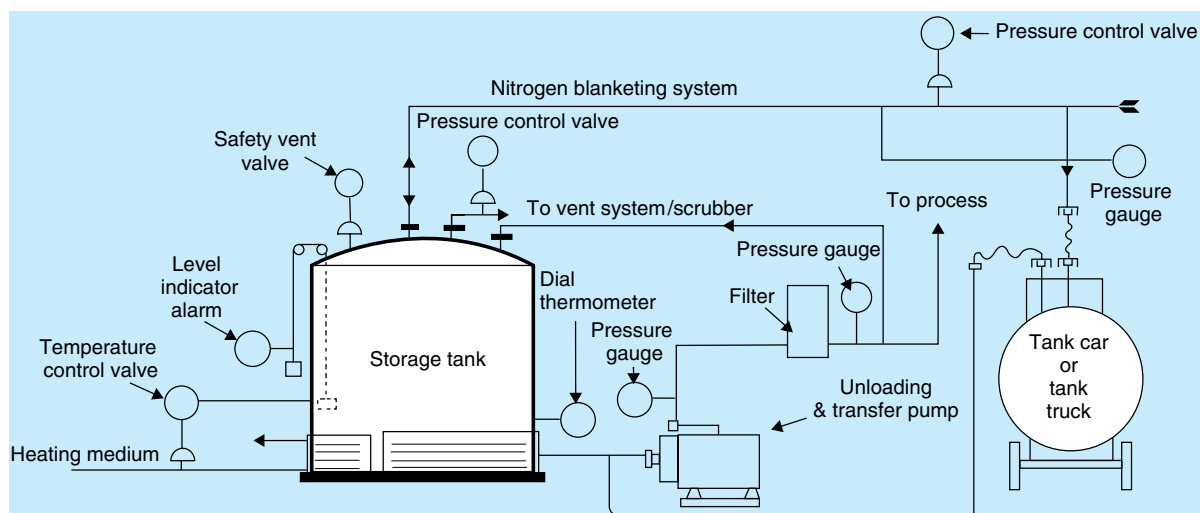


Figure 2.23 Typical diisocyanate bulk storage system

and the design must include a top mounted agitator or other means of preventing local over-heating. Heat exchangers may also be used. They should preferably be electrical or circulating hot oil yielding a maximum temperature of 70 °C (158 °F). Steam heating is not recommended as it may overheat the diisocyanates. Typical storage temperatures for MDI and for TDI are given in Table 2.8.

Table 2.8 Typical storage temperatures for MDI and TDI.

| | Typical storage temperatures | |
|---------------|------------------------------|------------|
| | °C | °F |
| Pure MDI | | |
| as liquid | 40 to 45 | 104 to 113 |
| as solid | –20 to 0 | –4 to 32 |
| Polymeric MDI | 15 to 25 | 59 to 77 |
| TDI | 15 to 25 | 59 to 77 |

Polymeric MDI should not be held at 70 °C (158 °F) for more than 4 h. It is beneficial to have provision to circulate the diisocyanate to achieve a uniform product temperature. It is recommended that tanks be equipped with temperature monitoring systems that record the actual temperature of the product in the tanks. Skin thermometers are not recommended as they do not accurately measure the product temperatures. Temperature alarms with high and low warnings are recommended. Monitoring is required to detect high temperature excursions which are typical of diisocyanate contamination with water. Additionally, it is important to control the temperature of the isocyanate because processes are sensitive to product temperature excursions, which in turn could give rise to

safety problems. The high temperature alarm should be set above the recommended storage temperature by 10 °C (18 °F) for polymeric MDI or TDI, and above the maximum recommended temperature for pure MDI by 6 °C (11 °F). If the tanks are located indoors, and if sufficiently high ambient temperatures can be maintained, jacketing may not be required for polymeric MDI and TDI.

MDI and TDI in storage tanks may be blanketed with dry air or nitrogen. Carbon dioxide alone is not recommended because of its solubility in MDI and TDI. Whichever blanketing gas is used, the water content should not be greater than 65 ppm (dew point of -40 °C, which is also -40 °F). This level can easily be achieved with both nitrogen and factory air dried by use of an in-line desiccant. Air entering a storage tank should be at working temperature. If it is hot it may purge the moisture from the desiccant and transfer it to the diisocyanate. This may be a problem when air from a compressor is used. Instrumentation for detecting the failure of the drying equipment for the purge gas is recommended. Compressor air must be oil free.

Lines leading to and from a storage tank should be constructed of similar materials to those of the storage tank and should be capped tightly immediately after use. This will prevent moisture from coming into contact with residual diisocyanate in the lines. Gaskets used in the transfer from a tanker should be replaced each time a transfer is made. All pipework should be insulated and traced where appropriate. Marking of MDI and TDI tanks, piping and connections should be clearly identifiable. The pipe joints must not be threaded, but welded or flanged. Flexible hoses are required to make connections to the tanks. Hoses made from braided stainless steel lined with nitrile rubber or fluoroelastomers are suitable for low or medium pressure duty.

Storage tanks should be fitted with devices to prevent over-filling. These devices detect the level of the contents and provide an audible and/or visual warning when a predetermined level has been reached. The system then shuts the inlet valve and prevents further ingress of material. An alarm to indicate low levels should also be fitted. Sight glasses should not be used as the only indicator of liquid levels. If they are installed they must be protected against accidental breakage and installed in a manner not to permit complete drainage of the tank should they become damaged. Electronic devices are more suitable.

Diisocyanate may be transferred from the storage tanks by pumps. The pumps should be immersed (for example in liquid paraffin) or canned. Seal-less canned pumps are recommended due to their ability to contain the material during pumping without leakage. While magnetic drive pumps are more expensive, their service-free extended life makes them more desirable for diisocyanate use. Strainers should be installed on the suction side of the pump to prevent damage to the impellers from foreign bodies or solids. Pressure gauges should be installed on the discharge side of the pump. All drain valves installed should remain plugged or capped when not in use. The pumps should be installed within the bund area and elevated for access at all times.

Filters should also be installed down stream from the pump and located in the containment area. The filters should be elevated to promote ease of draining and depressurization before opening. Drain and vent valves should be placed on the filter housing and equipped with caps/plugs. Pressure gauges installed on both the input and output side of the filter allow partial or total blockages to be detected.

Tanks must have vacuum valves that allow the ingress of nitrogen or dried air when the liquid level falls. These provide excellent protection against tanks imploding during product transfer. It is essential that all tanks have some venting arrangements to allow small changes in pressure to be normalized, with the vent outlet fitted with a carbon cartridge to adsorb MDI or TDI from the released air. Emergency relief venting of diisocyanate storage tanks also needs to be considered, given that activation of the system should occur only in most unusual circumstances. Worst-case scenarios should set the design requirements. Relief valves contain the diisocyanate once the design pressure is established in the tank. However, because atmospheric moisture may react with diisocyanates in a relief valve to form solid polyureas and so jam the valve, rupture discs should also be fitted at the outlet and the inlet of the valve. At the inlet, the disc material should be as specified for use with the diisocyanate and the setting should be close to that of the relief valve itself. At the discharge side, the disc should be set at a very low pressure. Additional emergency venting can be accomplished by the installation of a valved vent line. Regular inspections should be made of the tank and the relief valve/rupture disc arrangements. A pressure sensor and indicator should be located between the tank-side disc and the relief valve.

Transfers from storage tanks will necessitate the breaking of lines from time to time, with the need to contain the contents safely. Personnel involved in this work must wear protective clothing and have neutralizing materials readily available. Where lines are disconnected and reconnected it is very important that safety devices are installed to prevent inadvertent reconnection of the wrong lines. The consequences of accidentally cross-loading diisocyanate into a polyol tank, or vice versa, can be extremely severe and can cause a major incident. The most effective way of preventing incorrect discharge is to use different couplings (size and type) which are labelled to indicate the diisocyanate and polyol lines. However, it should not be assumed that the use of different couplings is a foolproof way of preventing cross-loading. There have been numerous cases where workers, convinced that they were acting correctly, have modified fittings, which allowed cross-loading. Colour-coded hoses and tagging with appropriate labels are useful additional safety measures. It is essential that the physical safety devices are accompanied by staff training and rigorous operating procedures to prevent cross-loading.

Pure MDI is transported in bulk in the molten state and must be maintained between 40 and 45 °C (104 and 113 °F) at all times to minimize dimerization. If, on arrival, the temperature of the material in the tanks has fallen slightly below the recommended temperature, the heating system of the tanker should be used until the correct temperature has been reached. The temperature must be monitored carefully to ensure that it does not exceed 48 °C (118 °F). If the temperature has fallen well below the minimum temperature the supplier should be contacted for advice.

Dimerization can be a safety issue since formation of solid dimer can cause problems such as blockages. This reaction is temperature dependent and the rate of formation of the white insoluble dimer is minimized between 40 and 45 °C (104 and 113 °F) in the liquid state and below -10 °C (14 °F) in the solid state (see Figure 2.24). Therefore storage at ambient temperatures is not recommended.

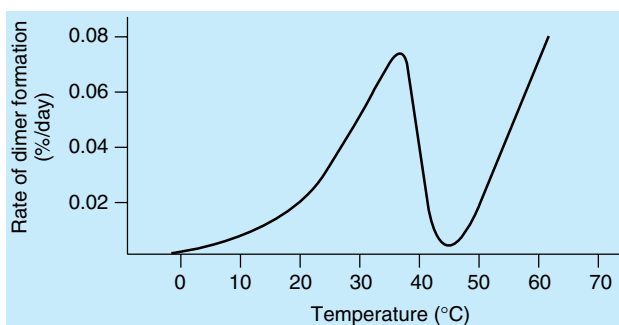


Figure 2.24 Pure MDI: rate of dimer formation. This diagram is based on information made available by BASF Corp., USA

Even at the recommended storage temperatures, slow dimerization will occur, resulting in cloudiness developing in the molten product. Table 2.9 (Dow, 1986) illustrates the approximate times, including the time in the supplier's warehouse and during transport, that pure MDI can be maintained at the given temperature before cloudiness develops. Users of pure MDI will, therefore, need to assure themselves that the material is not stored for long periods before use. In-line filters can be used to remove small amounts of solid that may have developed.

Table 2.9 Approximate storage life of pure MDI in the liquid state.

| Temperature | | Storage life days |
|------------------|------|----------------------|
| °F | °C | |
| 105 ^a | 40.6 | 31 |
| 110 | 43.3 | 35 |
| 115 | 46.1 | 35 |
| 120 | 48.9 | 28 |

^aAs this is essentially the melting point of pure MDI, storage at this temperature is not recommended.

Intermediate bulk containers

Re-usable intermediate bulk containers (IBCs), typically containing 1000 l, are commonly used for the delivery of both TDI and polymeric MDI. Pure MDI is not delivered this way because the IBCs are unheated and the MDI would solidify. The containers are used on-site for the storage of the diisocyanates and, when empty, are sealed and returned to the supplier for refilling. They are a very convenient way of handling diisocyanates for relatively small operations. The advantages include easy connections into processes and the simple return of the container for refilling without the cost and inconvenience of drum disposal. These containers have bottom run-off valves and can be connected up to machine tanks, thus avoiding the need to handle drums. A top-mounted dessicant cartridge dries the air that enters the container on discharge of the

diisocyanate. Diisocyanate suppliers should be consulted on the best type of container for a particular manufacturing situation.

Drums and pails: melting out

A considerable quantity of MDI and TDI is delivered to users in drums. The drums are predominantly of capacity approximately 200 litres (55 gal). Smaller containers (for example 1 gal pails) and cans of different sizes (for example 18 litres) are also available in different parts of the world. It is particularly important that the correct methods for handling, storing and using drums and cans are understood in order to maintain product integrity and to avoid releases of vapour or liquid.

Any warehouse used to store polymeric MDI or TDI drumstock should be well ventilated and, ideally, maintained at 20 to 25 °C (68 to 77 °F). The diisocyanates must not be stored with flammable materials, foodstuffs or corrosive materials. Drums should be stored palletized in an area that will contain any leaks; they should not be stored on earth floors. Drums should not be stored more than three high unless they are palletized.

Ideally, drums of polymeric MDI or TDI are stored inside to avoid extremes of temperature. However, if they are stored outside, exposure to direct sunlight and rain should be avoided. As drums of polymeric MDI or TDI may have been exposed to cold conditions during transport, the contents may be partially or completely solidified. Drums containing solidified material can be left in a warm room until the diisocyanate has melted. Alternatively, solidified polymeric MDI can be melted using the procedure described below for pure MDI. The contents should be well mixed before use.

Pure MDI is usually transported in drums in refrigerated containers at –20 to 0 °C (–4 to 32 °F) to prevent dimerization. Frozen drums should be stored immediately upon arrival in a refrigerated storeroom. A uniform temperature ideally below 0 °C (32 °F), and preferably lower, should be maintained. This will depend on the period of storage and the intended use. Temperatures must not be allowed to fluctuate widely if dimer formation is to be avoided. Drums of solid pure MDI should be used as soon as possible after delivery. Prolonged storage, even in refrigerated stores, can lead to a slow build-up of dimer.

Table 2.10 (Dow, 1986) shows approximate storage times for pure MDI in the solid state before cloudiness develops on melting. These times include the time the product has been in the supplier's warehouse and the time during transport assuming that the temperatures stated have been maintained.

Table 2.10 Approximate storage life of pure MDI in the solid state.

| Temperature | | Storage life |
|-------------|-------|--------------|
| °F | °C | |
| | | days |
| 0 | –17.8 | 300 |
| +10 | –12.2 | 210 |
| +39 | 3.9 | 68 |
| +50 | 10 | 33 |

Drums of solidified pure MDI, or products containing pure MDI, can be melted in a number of ways. However, because of the potential for dimerization, it is important to accomplish the melting procedure as quickly as possible whilst avoiding excessive local temperatures. The methods of heating pure MDI that are recommended by the manufacturers are the use of a hot-air oven, a steam chest or hot water bath. The highest heat transfer rate is obtained using a steam chest, hot water bath or a high humidity steam-powered oven. To improve the heat transfer and reduce the melting period, the drums may be rotated. When a hot air oven is used it should be well ventilated and the temperature should be within the range 70 to 80 °C (158 to 176 °F), or as indicated for the specific product in the product data sheet. Complete melting of the drum contents under these conditions may take up to 15 h. Electric drum heaters or other direct heating methods such as open flames or hot plates must never be used, as they would create local hot spots in the drums and hence excessive dimer formation. Whatever method of melting is chosen, drums should always be inspected carefully prior to melting. Any drum having significant damage should be marked appropriately and put to one side for later attention. If a drum bulges significantly because of excess internal pressure it requires emergency handling. Refer to *Key Theme 6, Dealing with accidents* for further guidance.

It may be necessary to provide a means of releasing any pressure that might build up during melting. A pressure relief valve may be used to prevent entry of moisture. This must have a carbon cartridge to adsorb emitted vapours. The valve must be inspected and cleared of any blockage prior to heating. A further option is to use a pipe nipple with a ball valve, but this needs to be opened manually to release pressure. Valves should be removed before the cooling of melted MDI in a drum is complete to prevent a vacuum developing in the drum.

The diisocyanate may be inspected with a light and, if necessary, stirred to confirm that no solids remain and that melting is complete. Atmospheric monitoring should be conducted at regular intervals to ensure that the extraction system is working efficiently. After melting, the drum contents should be mixed thoroughly to homogenize them; this may be achieved by rolling. The product can be allowed to cool to the correct processing temperature for polyurethane manufacture before use. If small-scale processing is intended, it is recommended that the drum contents should be melted and split into smaller quantities which can be frozen and melted out again separately when required. It is very important to homogenize the contents of the drum before splitting the contents. This procedure will prevent repeated melting and cooling of the product, and thus will minimize chemical degradation. Once a small quantity has been re-melted, it should not be further solidified and melted.

If a small quantity of finely-divided, insoluble material is present it may be removed by filtering through an in-line filter. A stainless steel vessel with a polypropylene filter bag is suitable. The lines should be heated and blown clear with nitrogen after use. Small amounts of finely-divided insoluble solids do not normally cause difficulties in handling or product performance.

Emptying of drums

The contents of diisocyanate drums are usually transferred to machine tanks or intermediate storage tanks. This should be done by using pneumatic (or

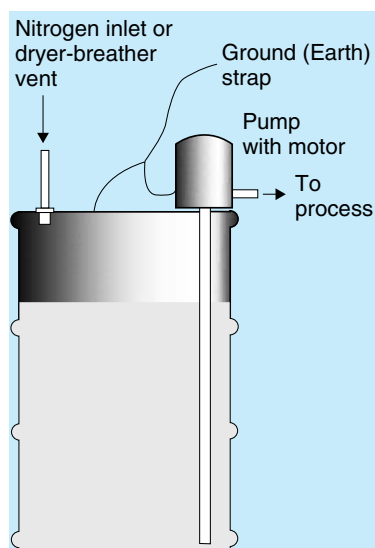


Figure 2.25 Drum unloading pump

electric) drum pump (Figure 2.25), or by using an electric standing pump with flexible dip tube inserted through the bung hole to minimize exposure. The area needs to be well ventilated and protective clothing should be worn.

Ideally, the drum pump or dip tube should be transferred direct from the empty drum into the contents of the next full drum, to prevent the ingress of air and moisture into the equipment. Drum pumps soon seize up if they are not protected from polyurea formation. It is not recommended that diisocyanates be poured direct from a drum into a tank. Spillage can easily occur even when there is lifting tackle.

It is very dangerous to pressurize diisocyanate drums to effect pressure transfer of the contents. Drums are not designed to withstand pressure transfer, and drum rupture may occur.

When drums are emptied with drum pumps or dip tubes, the back-flow from the dip tube, together with the residues on the walls and sides of the drum, can result in up to 5 kg (11 lb) of residual diisocyanate. If a nonreturn valve is installed at the bottom of the dip tube, the residual diisocyanate can be reduced to 400 to 1000 g (0.9 to 2.2 lb). Residues should be removed from drums before the drums are further processed. It is important to minimize the volume of the contents to facilitate their safe disposal.

Two suitable devices for draining drums and retaining their contents are shown below (Figures 2.26 and 2.27). Local ventilation should be provided and suitable protective clothing should be worn to prevent skin contact. In Figure 2.26 the inverted drum is secured in a frame. An attachment with a ball valve allows diisocyanate to be drained into the next drum of material to be used or a waste disposal container. The attachment screws into the bung hole of the drum and connects directly into a modified bung ensuring a tight fit with the receiving vessel. In Figure 2.27 the emptying device has a sloped platform provided with a protruding ring to allow central positioning of the drum and a funnel to receive the diisocyanate. The close contact of the ring

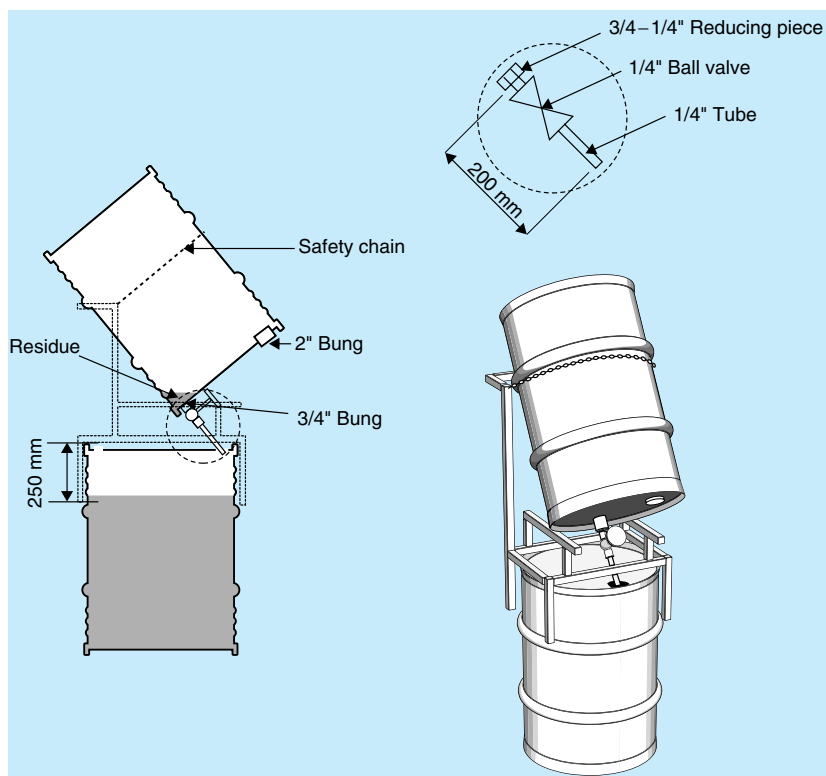


Figure 2.26 Emptying of MDI/TDI drums (1). Reproduced with permission from *Guidelines for the Responsible Management of Empty Diisocyanate Drums* (ISOPA, 1997)

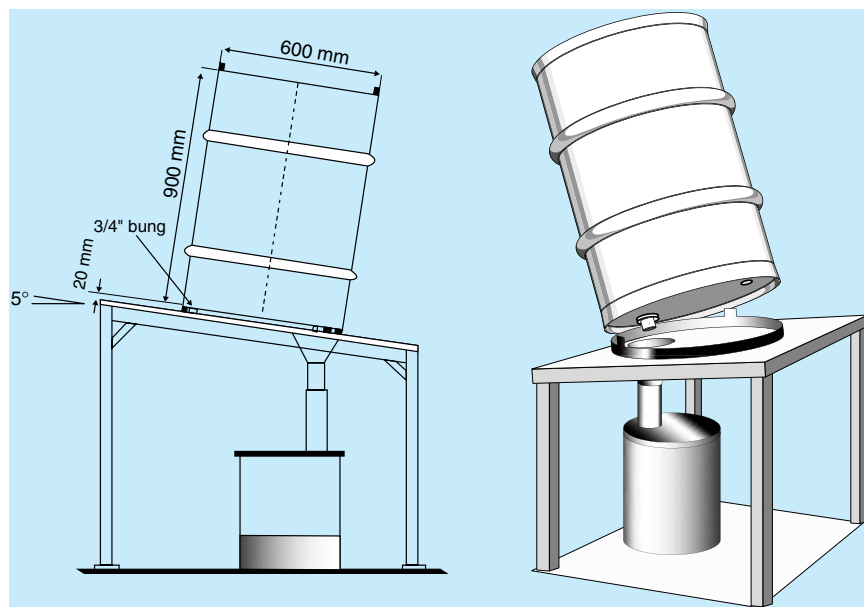


Figure 2.27 Emptying of MDI/TDI drums (2). Reproduced with permission from *Guidelines for the Responsible Management of Empty Diisocyanate Drums* (ISOPA, 1997)

and the open side of the drum prevents release of diisocyanate vapour during the draining process.

All drums should be drained at between 20 and 30 °C (68 to 86 °F) for about 2 to 3 h or until they are drip free. Pure MDI in drums should be drained between 45 and 60 °C (113 to 140 °F). This has to be done inside an oven and can generate a potential vapour risk. After thorough draining, the drum will retain residues of about 60 g of TDI or about 300 g of a highly viscous MDI prepolymer as shown in Figure 2.28.

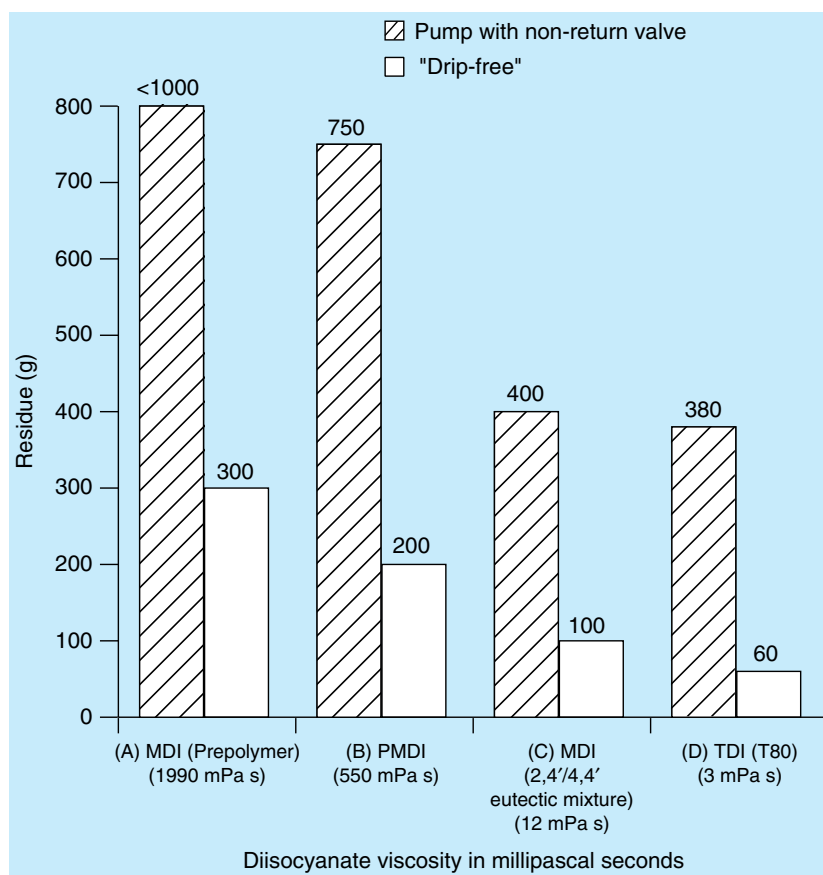


Figure 2.28 Drum residues from four diisocyanates at 25 °C. Reproduced with permission from *Guidelines for the Responsible Management of Empty Diisocyanate Drums* (ISOPA, 1997)

Empty drums should be well sealed to prevent moisture ingress, until they are processed further. This may involve sending them to a specialist drum processor or decontaminating them locally: in either case the original label should be left on the drum to advise the workforce of potential risk of handling. See *Key Theme 3* for details on drum decontamination. Empty drums should be inspected regularly for signs of pressure. If a drum is found to be bulging it should be treated as a potential emergency. Immediate action should be taken as indicated in *Key Theme 6: Dealing with accidents*.

Taking samples

If a small sample of diisocyanate is required for quality assurance, it should be provided by the manufacturer. However, if it is necessary to sample a small quantity of diisocyanate from a drum, it can be drawn off conveniently by positioning the drum horizontally and using gravity discharge. The method is described in the box. Once a drum has been opened, adequate precautions must be taken to prevent the entry of moisture.

Taking samples from a drum

Stand the drum head uppermost. Remove the two seal caps and remove the 3/4 inch diameter bung. To the 3/4 inch bung hole fit an elbow of piping, with a hand-operated valve to contain the contents of the drum during tipping, and a silica drier to prevent water ingress. Remove the bung from the 2 inch diameter bung hole and fit a gate valve or PTFE-lined diaphragm valve. With the valve closed, lower the drum into the horizontal position on to a suitable drum stand or trolley. A drip tray containing solid absorbent and adequate supplies of liquid decontaminant should be available. A bund (dike) to contain spillages is desirable.

Safety issues in workplaces using MDI and TDI

MDI and TDI are used in many different types of polyurethane manufacturing processes. Most such processes involve the mixing and dispensing of carefully measured quantities of reaction components, comprising a diisocyanate, and a polyol with other ingredients such as catalysts and surfactants. These reaction components are

measured and mixed, continuously or discontinuously, using high pressure impingement mixing heads or low pressure mechanical mixing heads, or by batch mixing techniques. Several common polyurethane manufacturing processes are illustrated in Figure 2.29.

The three principal ways in which workplace exposure to emissions of MDI and TDI can be minimized are by:

- good engineering design of the equipment and the systems used to handle the diisocyanates, to minimize releases;
- the use of appropriate ventilation systems;
- good working, housekeeping and waste disposal practices.

Good engineering design

Processes should be designed for:

- safety;
- minimization of releases and pollution;
- compliance with regulatory requirements;
- smooth throughput of products;
- ease of operation and observation;
- easy access for maintenance;
- easy access for charging tanks;
- simplicity;
- cleanliness;
- waste minimization.

Good design of manufacturing processes reduces breakdowns, maintenance, and process deviations and hence the need for operator intervention, resulting in reduced risks and reduced use of protective equipment. Good operational

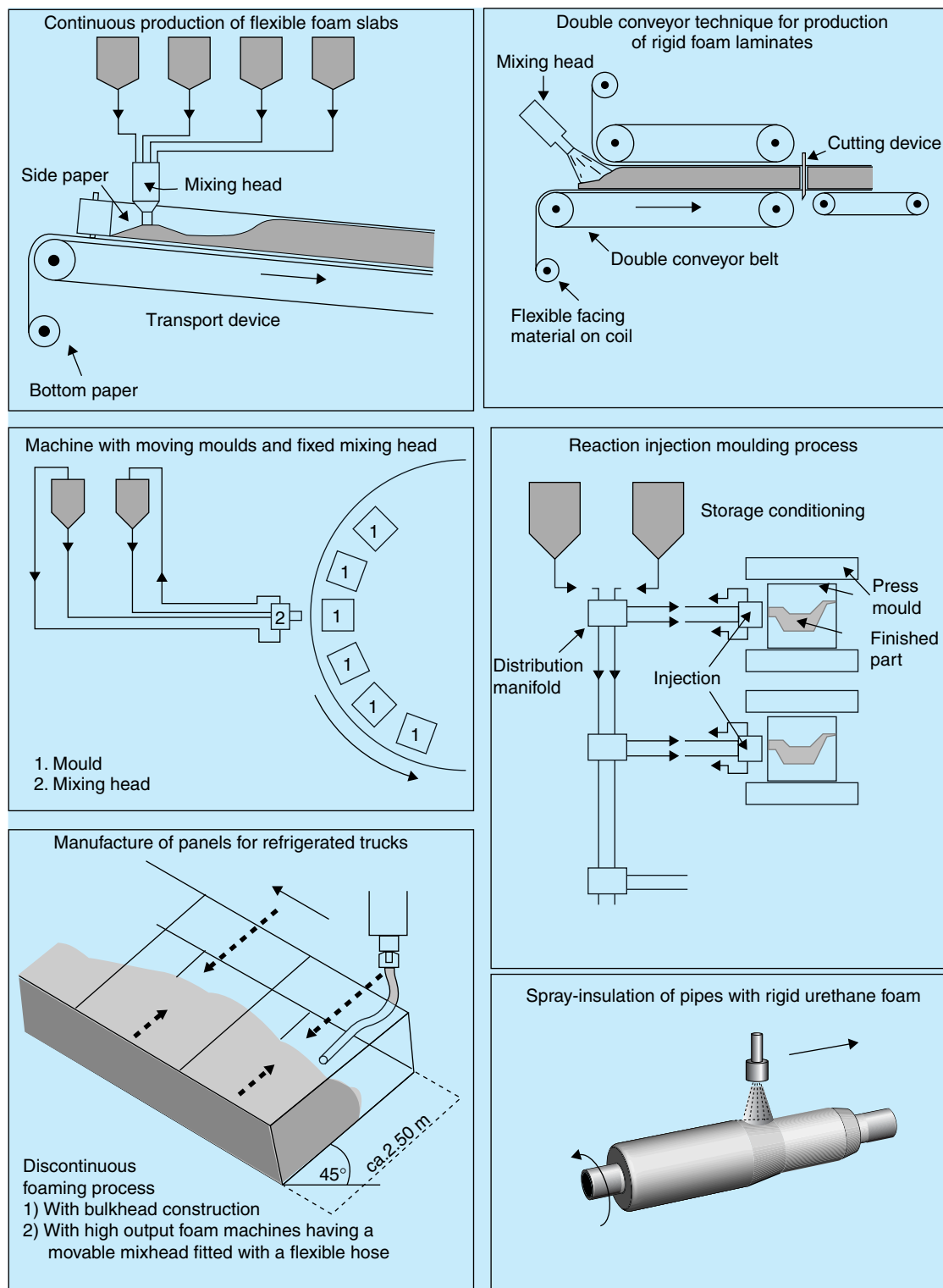


Figure 2.29 Some polyurethane manufacturing processes. Reproduced with permission from the handbook *Bayer-Polyurethanes*, 1979

procedures eliminate the need for operators to work in areas of high diisocyanate concentration. There can be considerable saving in effort and money if a safety measure is an integral part of the design rather than an additional highly instrumented system requiring its own separate maintenance, training and supervision. If a risk is identified it is always worth reviewing the basic design that gives rise to that risk, to see if the risk can be removed at source. Engineering solutions should be sought for plants that require workers to enter enclosed areas frequently. This may mean, for example, designing external controls, using more reliable seals and gaskets and provision of automated sample taking rather than adding a ventilated enclosure for manual sampling.

Liquid releases may be minimized by:

- Using closed liquid transfer systems from bulk storage to the processing machinery. In-line metering of chemicals removes the need for manual weighing.
- Using glandless, canned or fully immersed pumps to minimize leakage.
- Installing pumps and other items of equipment in positions for easy access for maintenance.
- Ensuring that lines transferring chemicals have a minimum number of joints. Joints should not be threaded, and they should be provided with spill protection where necessary, since leaks can sometimes occur at joints.

Pipework for MDI and TDI transfer should be all-welded with bolted flange connections using gaskets of Viton[™], Teflon[™] or nitrile rubber where practicable. Manual feeds should be minimized. Feed valves should be interlocked to prevent mis-feeds, mis-sequencing of raw material stream or spillage of the mix. For liquid leaks, such as those caused during disconnection of lines, hoses and filters, there need to be drip trays, bins, sealed floors or other measures. Filters and connections should be within their own enclosures and provided with local exhaust ventilation.

Ventilation control

Control of diisocyanate vapours and aerosols is usually carried out by means of a suitable exhaust ventilation system. To minimize worker exposure to MDI and TDI vapour releases during the processing of polyurethanes, it is desirable to enclose the processing equipment as much as possible and to remove the releases by adequate ventilation. Good enclosures and properly designed covers, and segregation of parts of the process by internal screens, allow the principal sources of releases to be localized, so that the ventilation system can be kept to a minimum size, complexity and cost and still be efficient. Ventilation can be considered in terms of the following three categories:

- total enclosure, with local ventilation if necessary;
- partial enclosure, with local ventilation;
- no enclosure, with local ventilation.

There will need to be openings in all polyurethane processes. In a nominally fully enclosed manufacturing process, such as reaction injection moulding, the materials injected into the mould will displace air through vents. The displaced

air may possibly carry with it some diisocyanate vapour or aerosol. In the manufacture of flexible foam slabstock considerable quantities of diisocyanate will probably be present above the rising foam and these will need to be contained and removed. Full enclosure is not a practical option since most of the processes require openings in their enclosures to allow entry or exit of moving parts. In these cases the preferred choice is to enclose the process as fully as possible and use ventilation to control and minimize releases from the enclosure to the workplace. Extraction of contaminated air is most effective when a directed source of fresh air is also provided to ensure preferred directional air currents. Local ventilation will work best if it assists the natural flow of the vapours and aerosols, is close to their source, and is located so as to receive them. Broadly speaking, releases from warm moulds and warm rising foam will tend to rise with the associated warm air, while spray aerosols will tend to sink or travel with the air flow. The vapour density of the exhaust gas is virtually the same as that of air at the same temperature, as the diisocyanate vapour concentration is always extremely low. In a tunnel enclosure, the extract ducts should be located so as to give adequate inward flow through the openings while disturbing the process as little as possible. The ducts should be located to avoid producing a strong draught inside the enclosure over the rising foam unless it is required to remove fumes for other reasons, such as explosion control if certain solvents are present.

To maximize the removal of releases the exhaust ventilation used should be:

- inside a well-designed enclosure;
- placed so as to assist the natural direction of travel of the release;
- placed close to the source of the release;
- capable of dealing with jet flows.

The rate of air flow should be monitored and displayed.

Jet flows (fast-moving, directional air streams) carrying aerosols may arise in certain operations, notably in spraying but also in applications in which air is expelled rapidly from mould vents. To achieve highly effective extraction, it is essential to accommodate these powerful jet flows by aligning ventilation outlets with them. Moving machinery can also cause jet flows. Cooling fans on motors can create draughts. Disc and band knives can establish very strong jet flows as air is entrained by the moving blade. If necessary, smoke canisters or smoke candles can be used to establish the direction and speed of movement of jet flows.

For some processes options for enclosure are limited because of the space requirements for access or movement of parts. An example might be the pouring of reaction mix into open moulds mounted on a carousel. Partial enclosure requires more extraction than total enclosure because of the proportionately larger open face. The effect of increased air removal is to make it more difficult to control the temperature in a partial enclosure than in a full enclosure. Furthermore, the extraction has to be in the right place because, unlike full enclosure, it is unacceptable for the enclosure itself to be full of vapour.

Local exhaust ventilation without enclosure and general (dilution) ventilation are the least effective means of collecting and controlling releases. Additionally, where abatement or clean-up treatment of the exhaust air is needed before discharge to atmosphere, such ventilation provides the largest volume and most dilute mixture to the treatment plant. This increases the treatment plant size and running cost, and reduces its efficiency. The cost of heating air to replace the air extracted can also be very significant. However, if releases are known to be at a low level, local exhaust ventilation with or without enclosure and good general workplace ventilation can adequately protect workers (Figure 2.30).

Most enclosures are too small for entry, but operators may still be able to lean in. Access to a working enclosure should be restricted, or even prevented,

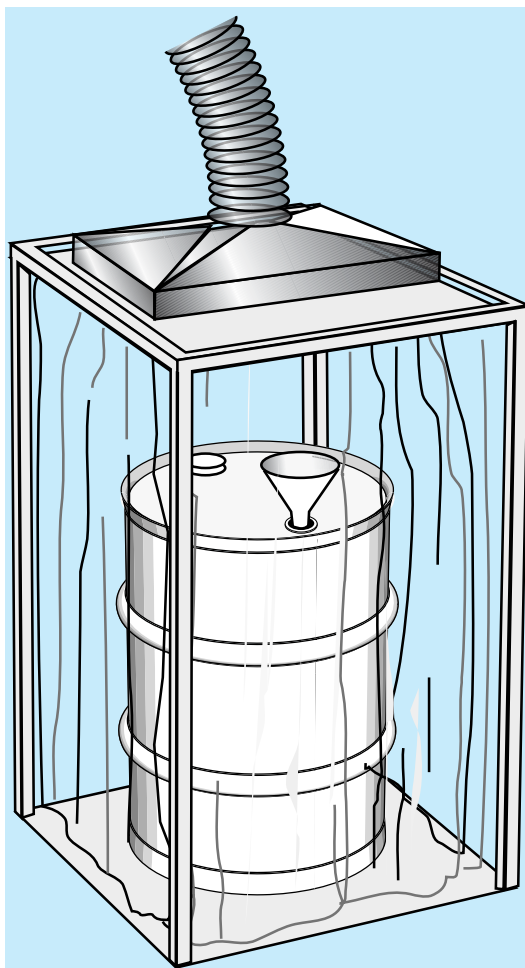


Figure 2.30 Local ventilation over a diisocyanate-containing drum

in normal use. When access is required for maintenance or other work there should be strict personnel control. Good visibility into the enclosure reduces the need for access, as does good process design. Processes should not require manual transfers of components into or out of enclosures.

Vapour releases from operations using MDI or TDI will be almost invariably at concentrations considerably lower than those of their saturated vapour, and hence not liable to condense in ducting. The duct velocity is not crucial, and the limit is likely to be defined by the balance of airflow noise, power loss in the ducting and excessive size of the ducts if the duct is enlarged to reduce noise and power loss. Some operations give rise to aerosols, particularly of reaction mixture. Design of ducting will need to take account of the presence and size of aerosol particles: the larger the particle the more likely it is to deposit onto sharp bends in the ducting. Where foaming mix is deposited on ducting polyurethane foam may collect and build up altering ventilation characteristics, and may even cause blockages over a period of time.

In cutting and trimming, where dust may be generated, the ducting can usefully incorporate a wider section and waste bin to collect heavier particles near

the source of the dust. The duct should thereafter have a diameter calculated to give a duct velocity of 10 to 20 m/s (2000 to 4000 ft/min) greater than the transport velocity of the dust produced. Where deposition of dust, solvent or aerosols of reacting ingredients is foreseeable, the ducts will need to have access for cleaning, and possibly drainage points.

The need for indicators of air flow will have to be judged in the light of current best practice, local legislation and the seriousness of the consequences of lack of ventilation control. One very simple device is a hanging strip of paper or fabric in front of the ventilation intake, although it shows only that there is some extraction flow. On modern block foaming plants enclosed in tunnels a fall in air flow, detected by pressure differential or other devices, raises an alarm and stops the chemical feeds. Such devices are becoming increasingly the standard on extracted spray booths.

Spraying polyurethane foam insulation in a confined, inaccessible area with only a low level of local ventilation available requires operators to wear a fully protective suit including supplied-air respiratory protection. Unprotected people should be excluded from the high exposure area until safe conditions have been established.

Good working, housekeeping and waste disposal practices

Good working practices

Mixing of the reaction streams in polyurethane processes can be achieved by low pressure mechanical mixing or by high pressure impingement mixing. In low pressure mixing equipment, a mixing head of a relatively large volume containing a rotating stirrer is used in order to obtain continuous efficient mixing of the components (Figure 2.31). In order to clean the equipment at the end of the dispensing operation all chemical streams can be closed down except the polyol stream, which then removes residues of all other chemicals. Alternatively the mixing head can be flushed through with a solvent to remove

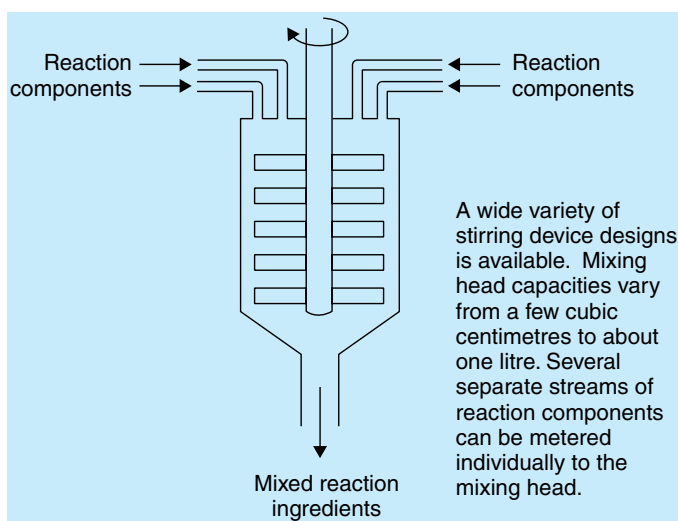


Figure 2.31 Low pressure mixing

any residual polyurethane material, followed by an air blast to remove the residual solvent. This action can lead to emissions of diisocyanates and solvent vapours. It is essential that all rinsing and cleaning operations are done into a container fitted with its own extraction facility. It is also strongly advisable to link the solvent flush and air blast, so that air cannot be put through a head before the solvent flush.

The alternative technology employs high pressure dispensing equipment (Figure 2.32). This technique uses piston pumps metering the chemicals under a pressure of 150 to 200 bar (2175 to 2900 psi). Mixing is carried out in a very low volume chamber where the atomized chemical streams mix by impingement. The mixing head is self-cleaning, being fully purged by means of a close fitting plunger at the end of each shot. One great advantage that high pressure mixing heads have over low pressure heads is that solvent and air blasts are not needed.

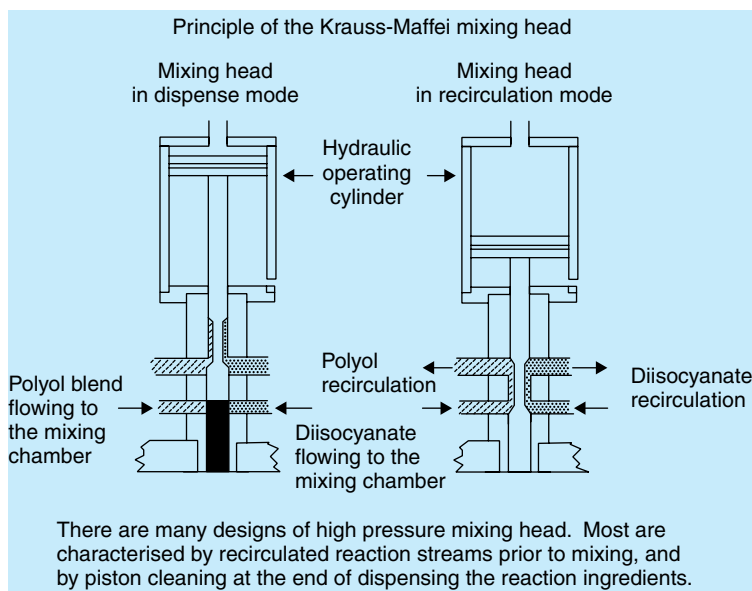


Figure 2.32 High pressure mixing. Reproduced by the kind permission of Huntsman International

Adequate personal protective equipment needs to be provided for all expected situations in the workplace, including emergency situations, and staff must be trained in its use. It is important for managers to ensure that the equipment is actually used, and that it is maintained.

As minor drips and leaks of diisocyanates are possible in a number of workplace operations, an adequate stock of neutralizer and absorbent solids for diisocyanates should be readily available and staff should know where they are and how they should be used. Neutralizer will also be necessary to deal with used drums, machine parts and contaminated clothing. Contaminated clothing must be changed immediately if it becomes contaminated with MDI or TDI to prevent skin contact. After spills and leaks are dealt with, workplace air should

be monitored to ensure that the occupational exposure limits for diisocyanates are not exceeded.

Maintenance tasks may take place outside normal working hours when there may be limited support available in case of problems. Maintenance, such as breaking open lines or dismantling pumps containing diisocyanates, can involve potential exposure. It is, therefore, particularly important that all staff involved in maintenance activities are made fully aware of the potential dangers, and are fully equipped with appropriate personal protective equipment.

Diisocyanates usually react very rapidly during polyurethane manufacture, particularly when catalysts are used. Despite this, very small amounts of excess MDI or TDI may remain unreacted during the curing process in foams and other products, and polyurethane products should be handled with caution until it has been established that no atmospheric or skin contamination occurs. In any event, it is important to wear gloves when handling freshly made polyurethanes to avoid possible skin contamination. Any residual diisocyanate usually disappears due to completion of the polyurethane reaction, by reaction with atmospheric moisture or by reaction with the polyurethane itself. TDI was not detected when air was passed through cured flexible foam for bedding that had been made for 3 days, even when extremely sensitive tests were used (Hugo *et al.*, 1997).

During the period of final cure, finished products should be stored in well-ventilated areas unless it is known from air measurements that the diisocyanate is no longer being liberated. Polyurethanes made in large blocks, such as flexible foam slabstock, may retain heat for many hours because of the insulating properties of the foam. Such blocks should not be stored close to each other to allow heat dispersion, and fire prevention systems must be installed. If post-manufacture fabrication is undertaken on freshly made polyurethanes, workers should be protected from possible diisocyanate exposure by ventilation of the workstations.

Local measurements of diisocyanate concentrations in the air should be carried out if there is any doubt about the need for supplementary ventilation. In addition to diisocyanates, there will often be additives in the polyurethane formulation such as catalysts, including tertiary aliphatic amines, fire retardants, surfactants and blowing agents. Some of these substances may also be sufficiently volatile to add to the ventilation requirements necessary in the storage and fabrication areas, particularly in the case of open-cell flexible foams.

There are several industrial operations in which cured polyurethanes may be subject to degradation due to the effect of heat (thermolysis). These include:

- hot wire cutting of flexible foam;
- hot air welding of flexible foam and polyurethane elastomers;
- flame lamination of flexible foam;
- sawing of rigid foam;
- sanding of rigid foam.

Gaseous breakdown products resulting from thermolysis have been studied, see, for example, the abstracts of the Isocyanate 2000 Symposium (Isocyanate 2000, 2000). The dusts from some of such operations have been analysed for residual isocyanate groups. This is a complex field, with many outstanding

questions on analytical methodology, the effect of different thermolysis conditions, the formulae of the foams and associated risk assessments.

Those involved in such operations should be protected from exposure to thermolysis gases and dusts by the use of effective engineering measures to minimize exposure, but preferably by changing the process to achieve the effect without thermolysis. For example, hot wire cutting has been replaced by sophisticated cutting devices such as band saws, oscillating saws and high pressure water jets, from which levels of emission breakdown products are extremely low.

Exposure to toxic combustion gases can arise from polyurethanes being burned in unsuitable devices. Diisocyanates may be released from burning polyurethanes, in addition to the normal and expected combustion gases (i.e. carbon monoxide, carbon dioxide, nitrogen oxides and hydrogen cyanide) from any natural or synthetic material containing carbon and nitrogen, such as wool, silk, nylon and acrylic fibres, and ABS. Accordingly, all incineration should be carried out by specialist companies. It is important to ensure that polyurethanes are not allowed to burn in open fires.

Good housekeeping

Good housekeeping requires working procedures, training and resources to be both provided and implemented as part of the safety system to ensure clean working conditions and the adequate maintenance of production and safety equipment.

- Define limited areas where diisocyanates are stored separated from other chemicals. It is important to isolate the diisocyanate storage areas from the polyurethane production areas.
- Ensure that MDI and TDI are always stored in clean, closed containers.
- Ensure that every drum is correctly labelled and that the label clearly describes the contents.
- Minimize the number of partly used drums.
- Prohibit eating, drinking or smoking in the workplace where diisocyanates are used: separate areas should be provided. Encourage personal cleanliness, especially when taking a break from work.
- Keep machinery and other equipment clean and decontaminated when not in use. Solvents that are increasingly used to clean contaminated equipment include *N*-methyl pyrrolidone and 'dibasic ester' (a technical product made from mixed dibasic carboxylic acids). If solvents are used during the cleaning process, prevention of skin contact is particularly important.
- Traces of diisocyanates should not be left on work surfaces, floors or external machine parts. They may contribute to inhalation exposure, or cause skin contamination.

Good waste disposal practices

Decontamination of drums

This should be undertaken as soon as possible after removal of the contents. Drums must be drained before decontamination, and then stored upright for at least 2 h to allow product to drain from the drum wall to the bottom. Drums

should be decontaminated at 20 to 25 °C (68 to 77 °F). Diisocyanates having a viscosity of greater than 150 mPa·s, such as polymeric MDI and prepolymers, should be maintained at 25 to 30 °C (77 to 86 °F). Pure MDI must be neutralized at 45 to 60 °C (113 to 140 °F). An oven should be used for warming the diisocyanates. Diisocyanates are neutralized as described in *Key Theme 3*.

Decontamination of drums

Drain drum until drip-free



← Add neutralizer liquid (see *Formulations 1 and 5* in *Key Theme 3*)

Roll the closed drum at least four times



Open drum (CAUTION: excess pressure may be present!)
and leave with a loose-fitting lid until all the reaction
is completed.



Close drum and dispose of contents and drum in approved manner

Once drums are decontaminated and all reactions have ceased the drums should be closed tightly. Labels should be attached indicating the contents of the drum and its status as decontaminated. A certificate of drum decontamination accompanying the drums to the reconditioner is strongly recommended (see *Key Theme 3*). Drums that have been decontaminated will contain neutralized diisocyanate, and residual neutralization solution and can be handled by a specialist drum reconditioner or metal recycler. Decontaminated drums may be used for scrap metal, or may be reused after reconditioning. As a last resort they may be sent to landfill after removal and safe handling of the waste neutralizate. Drums for landfill should be punctured or crushed before disposal to prevent re-use. The re-use of drums that have not been completely decontaminated is potentially very dangerous. For example, the re-use of TDI containers to transport nontoxic materials is reported to have led to illness in 40 workers in a plant making surgical gloves from rubber latex (Siribaddana *et al.*, 1998). Used drums, even if believed to be diisocyanate free, must never be used for domestic purposes such as a barbecue, domestic incinerator or trash receptacle.

Under no circumstances should hot torches be employed to cut up used drums, since such drums may contain residues of MDI or TDI.

In many countries there are qualified drum reconditioners and recyclers who will clean the drums before reconditioning, or who will reclaim the drum for

Sources of information on drum reconditioners are: European Federation of Drum Recyclers, SERRED; The Association of Container Reconditioners (USA).

its metal content. It is important to select a company that has the full local and national authority approvals necessary for processing and disposal of waste product residues, and for the transport of the drums.

Diisocyanate suppliers may be able to provide the names of suitable companies. When possible, the company should be audited and approved for drum reconditioning or recycling. The methods used for disposal of waste residues should also be examined. Regulations and commercial practices vary from country to country. Local enquiries should be made before drum disposal procedures are established.

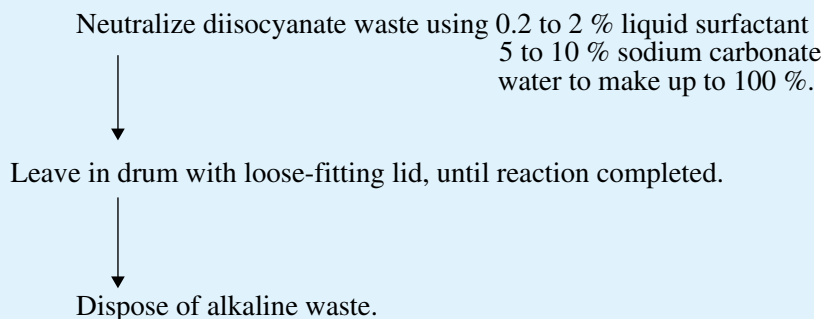
Disposal of diisocyanate waste

Waste diisocyanate may be collected until there is a sufficient quantity for disposal by a specialist contractor. However, a small amount may be conveniently handled on site. There are three basic methods of disposing of liquid diisocyanate wastes. These must be considered in the light of local regulations. The choice of method will also depend upon the amount of waste to be treated. The methods below are discussed in *Key Theme 3* in more detail.

1. Reaction with liquid neutralizing agent

The diisocyanate is added slowly to the neutralizing agent while stirring in an open-topped vessel such as a drum. To ensure a complete reaction the proportion of neutralizer to diisocyanate should be 9:1. Any waste solvents containing diisocyanates must also be treated to neutralize the diisocyanate before the solvents are disposed of.

Disposal of diisocyanate waste



2. Incineration

This should be carried out only in properly supervised facilities specifically designed for the disposal of noxious chemical waste.

3. Reaction with waste polyol blend

This is normally used only after machine calibrations when the metered amounts of diisocyanate and polyol blend can be reacted together to give a polyurethane. This should be undertaken with great caution (see *Key Theme 3*).

Safety issues in some important polyurethane processes

Flexible polyurethane foam slabstock production

The flexible foam slabstock process (Figure 2.33) is an excellent example of the continuous developments in engineering control, which have led to reduced releases into the workplace. In this process, the foam mix is dispensed onto a carrier paper on a conveyor which draws it through a ventilated tunnel with the rising foam. As the foam rises it is contained within side-papers running along sidewalls. Once the block is self-supporting, all papers are removed and disposed of. Innovations in the process which relate to safety have been the use of a top paper and the use of polythene sheeting between the rising foam and side-papers. The former reduces releases of TDI vapour from the foam surface. The latter prevents uncured flexible foam, with high TDI levels, from soaking into the paper. The handling of such saturated papers can be a significant source of potential exposure of workers to TDI. When polythene sheeting is used it does not need to be removed until the foam has cured. The ventilated tunnel has openings at the start and exit to accommodate the paper feed and conveyor with the emerging foam block.

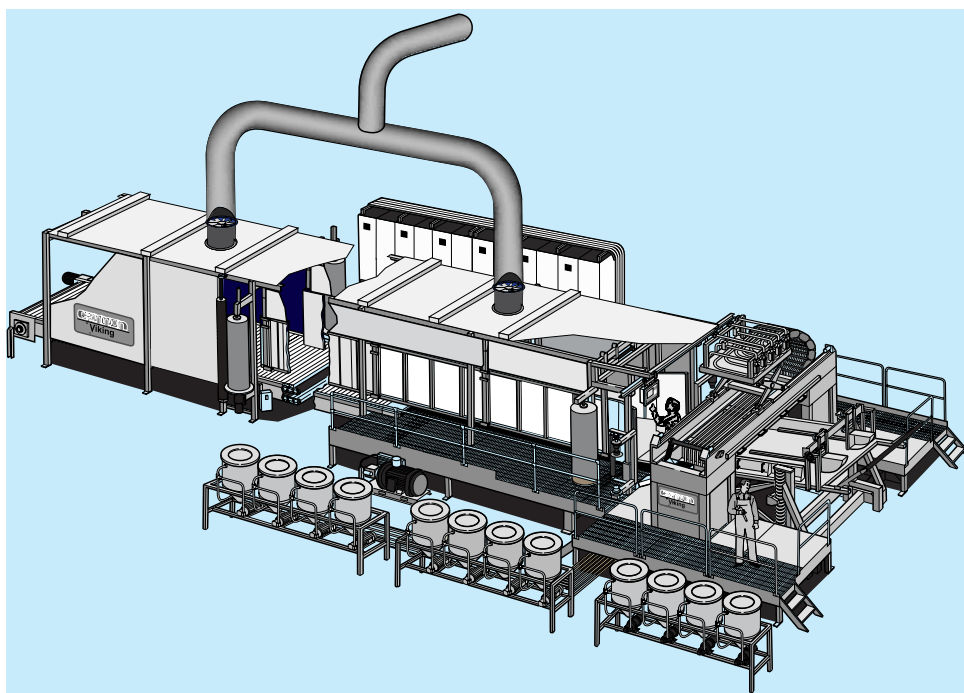


Figure 2.33 Flexible polyurethane foam continuous block plant (figure by courtesy of Cannon Viking Limited, UK)

Openings for inspection and sampling should, wherever possible, be self-closing or linked to an alarm warning system or both. There should be extraction on the tunnel enclosure applied near entry and exit so as to provide an adequate inflow of air at the openings. The extraction air flow depends on the process parameters, such as the size of openings, the rate of chemical throughput and the rate of rise of the foam. It should be, typically, at least

0.3 m/s (1 ft/min) inward for well-designed small openings liable to be open at any time. A higher airflow rate, 0.5 to 1.0 m/s (1.6 to 3.3 ft/min), is appropriate for large openings close to vigorous sources of emissions. Only a small quantity of diisocyanate vapour is emitted at the pouring point or trough. However, at this point a very large volume of air is being drawn into the extraction system and this prevents escape of airborne diisocyanate from the head of the tunnel.

The enclosure should be well lit internally so as to reduce the need for observers to approach windows or openings too closely. Operators require access before and after each run to service the mixing head, but during runs direct observation may be achieved through windows into the highly illuminated tunnel or by closed circuit TV cameras. Note that if the lighting is through transparent panels from external light sources, the cost of the installation is reduced and it is much easier to clean and maintain. Workers should not touch nozzles, or enter the foaming tunnel enclosure, or deal with the paper removal without extensive personal and respiratory protection.

The efficiency and effectiveness of an enclosure can be improved by attention to design detail. The number of openings should be minimized and the risk of turbulent air currents of contaminated air escaping from the main foam entry point can be reduced by profiling the opening so that there is a smooth transition into a short entry tunnel. Waste bins should be incorporated inside the enclosure to contain any waste generated. Sometimes a negative pressure indicator or loss of negative pressure detector is installed in the tunnel to give a warning alarm.

Flexible foam slabstock can also be made discontinuously (Figure 2.34). Here also excellent ventilation arrangements are necessary (not shown in the figure) to protect workers from exposure to diisocyanates.

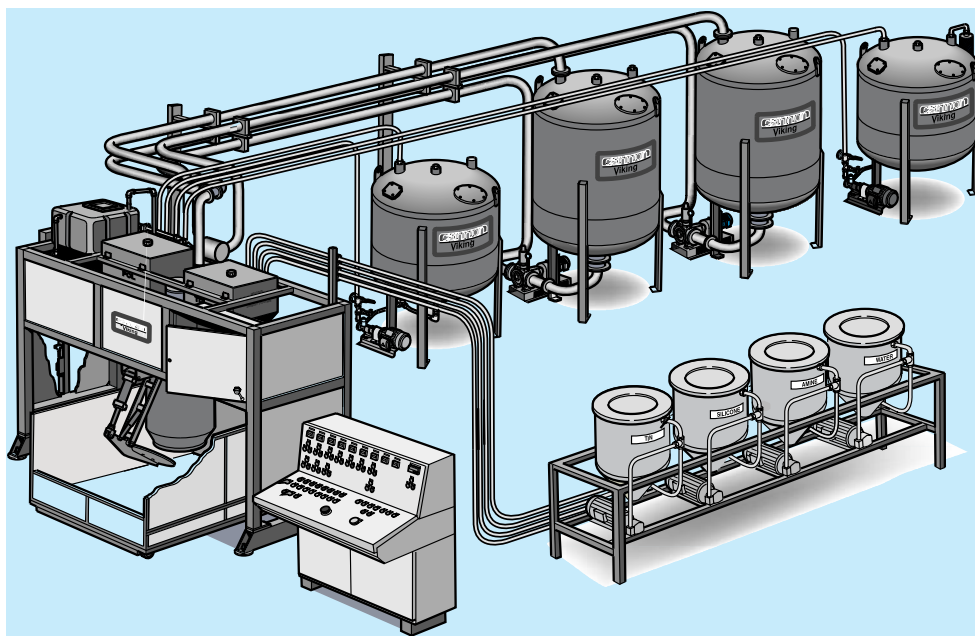


Figure 2.34 Flexible polyurethane discontinuous block plant (figure by courtesy of Cannon Viking Limited, UK)

Polyurethane foam moulding processes

A typical example of this type of process is polyurethane foam moulding where open moulds are transported past fixed operating stations (Figure 2.35). A production cycle consists of

- cleaning the mould;
- spraying on release agent;



(a)



(b)

Figure 2.35 Car seat moulding line: (a) polyurethane mixing head above an open cushion mould; (b) operator removing polyurethane cushion from mould. Figures reproduced with permission from British Vita Plc

- dispensing the reacting polyurethane foam mixture into the heated mould;
- closing the mould;
- allowing the foam to cure, sometimes in a heated tunnel;
- removing the moulding from the mould, often aided by a compressed air gun.

Efficient ventilation (Figure 2.36) is needed when applying release agents, dispensing the polyurethane mixture, closing the mould and demoulding. There continue to be improvements in mould release technology, notably in a reduction in the frequency of application of release agent and the use of water-borne, rather than solvent-borne, systems.

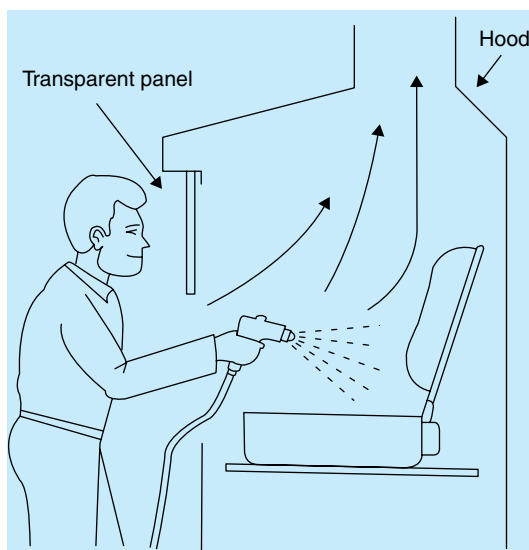


Figure 2.36 Spraying of release agent into a mould

Low pressure mixing heads need to be cleaned at intervals and sufficient ventilation is also required for this operation. High pressure mixing heads would not normally need to be cleaned. When moulds are used there may be a brief potential exposure peak as the mould lid closes, particularly when TDI is used. It is important in this case to provide ventilation at this point. To provide sufficient ventilation at all these stages of the process requires careful design of the enclosures, including limiting the need for access for manual operations. The mould can be closed automatically or by remote control, and transported through the curing tunnel. The cured foam can be demoulded remotely. Operator contact with the process can thus be minimized and exposure to the possible emissions reduced. The highest potential exposure of operators is liable to be at the stages of dispensing, mould closure, the displacement of air from the mould during foam rise and manual demoulding.

Reaction injection moulding (RIM) in closed moulds is also widely used, particularly with fast-reacting MDI-based systems. In this process the reaction ingredients are mixed by high pressure impingement. The high pressure mixing head is an integral part of the closed mould and the reacting ingredients are injected into the mould cavity. A vent hole allows air to be displaced from

the mould. The moulds may be stationary or may move mechanically to the mixing head. Worker exposure to the reacting chemicals during RIM processing is extremely low. Care is usually necessary on demoulding the finished parts, though fast reacting systems have very little free MDI on demoulding.

Production of rigid polyurethane foam panels by a continuous process

In this process an MDI-based rigid foam reacting system is deposited onto a continuous moving substrate such as paper or steel. The foam mixture reacts and rises, comes into contact with a second facing material and forms a continuous polyurethane foam laminate (boardstock). The facing materials are often heated prior to contact with the foam mix to improve surface cure, increasing the potential exposure.

The even distribution of reacting foaming mixture on the substrate is critical to the process because the mixture expands to typically 30 times its initial volume. Originally, the best method to achieve such a layer was by means of a traversing spray head. This produced aerosols and splashes of reacting chemicals, which resulted in risks to the operators and could lead to deposits in ducting which had to be removed frequently. Engineering solutions have been found to overcome these problems. A pour laydown using a traversing pipe is now commonly used. This technique produces narrow bands of reacting liquid foam, which merge together during the ensuing process, eliminating splashing and aerosols. In another approach the foam mix is enclosed between the two facing materials before it begins its reaction. Due to the complete enclosure of the reacting foam between the facing materials, MDI emissions are greatly reduced. It is still necessary to enclose the foam laydown and conveyor area in a ventilated tunnel.

Spraying of polyurethane systems

Two-pack diisocyanate-based paint spraying and rigid foam insulation are typical examples of diisocyanates in spray applications. These applications are often carried out in controlled factory environments where engineering precautions can be taken to prevent worker exposure. Certain applications of rigid foam spraying have to take place away from a factory and special precautions will be necessary to protect those involved. Care must also be taken to avoid exposure of those not involved in the operation such as local residents and building occupants.

In a factory situation, the object to be coated can often be fully enclosed in a spray booth so that optimum ventilation can be applied to give excellent protection to the operator. The reacting aerosols need to be removed from the exhaust air by filtration before the air is discharged to the outside atmosphere. A water curtain may also be used to remove overspray.

Some of the best designs of spray booth provide laminar airflow across the opening and allow operators freedom of movement whilst protecting them from aerosols or spray droplets (Figure 2.37). All spray booths must be monitored at regular intervals to ensure that the enclosure and ventilation are fully effective. Ventilated enclosures are used, which protect those in the vicinity, when very large articles such as aircraft are sprayed inside a factory. Spray operators have

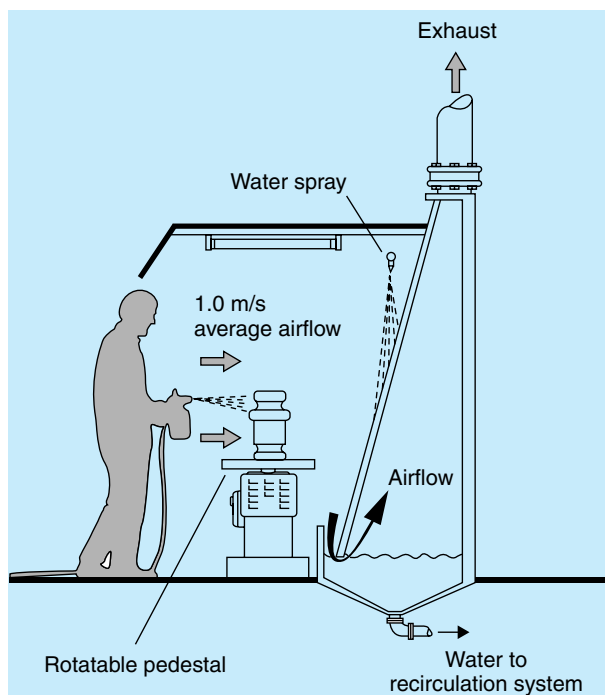


Figure 2.37 Water curtain spray booth. Figure reproduced with permission from *COSHH Essentials: Easy Steps to Control Chemicals, Health and Safety Executive, UK, 1999*

to operate inside these areas and must wear full protective clothing including positive-pressure, air-supplied respirators.

There are less controllable spray operations, such as on-site rigid foam spray insulation. Typical operations include the spraying of industrial roofing, external storage tanks, building steelwork, and domestic roof spaces. Although some of these operations take place in a closed environment, adequate ventilation is often not available because of the temporary nature of the operations. The only solution in all these cases is to use personal protection, including self-contained breathing apparatus (Figure 2.38). Only personnel trained in the work, or under close supervision, should be present.

Use of MDI and TDI in laboratories

Small-scale operations, such as quality control and formulation development, are carried out in laboratories. The handling of MDI and TDI in these situations demands the same care and attention to the control of exposure as on polyurethane manufacturing plants. Fume cupboards (hoods) with adequate air extraction rates need to be used for operations involving diisocyanates. If the laboratory equipment will not fit inside a fume cupboard, then larger ventilated enclosures will need to be provided. Personal protective equipment suitable to the situation will be required. This will normally be safety glasses, a protective overall or laboratory coat and impermeable gloves. All pouring, weighing and measuring of the diisocyanates should be carried out in well-ventilated fume

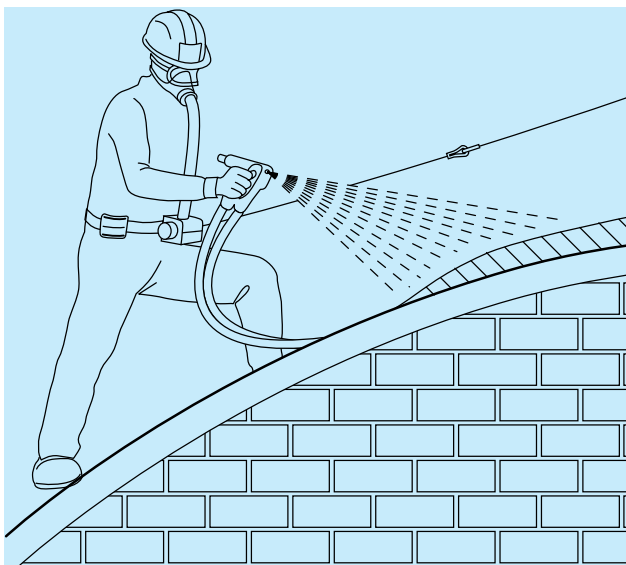


Figure 2.38 Hand-held spraying of rigid polyurethane foam

cupboards because open beakers or flasks provide situations for releases to air. The 'tack-free' times of rising foams should never be touch-tested unless gloves are worn. Diisocyanates must never be pipetted by mouth. Current laboratory practice is to use syringes to measure diisocyanates volumetrically. All spillages must be neutralized using the procedures already discussed in *Key Theme 3*. Eating, drinking and smoking should not be permitted in laboratory areas. Laboratory workers should receive routine medical surveillance in the same way as production workers (*Key Theme 2*).

Visitors to the workplace

Most safety procedures are designed primarily for those present in the workplace on a regular basis. It is important to recognize that visitors who enter areas where diisocyanates are handled and processed should be included in the safety system, as they may not know of the risks associated with over-exposure. Visitors will need to use the appropriate protective equipment, of course, and should be accompanied at all times. One approach to protect visitors is to have them read and understand relevant safety information prior to site entry. A possible text for recording that visitors have done this is shown.

INFORMATION FOR VISITORS TO DIISOCYANATE AREAS

MDI and TDI may cause adverse health effects, in particular respiratory problems.

No visitors should enter a diisocyanate area if they suffer from bronchitis, bronchial asthma, repeated attacks of hay fever, or any other lung disease.

It is suggested that if any person is visiting the Company for more than a single day or on more than a single occasion, screening by medical personnel should be considered.

Persons visiting the Company on a single occasion only, for a period of one day or less, may be permitted to enter diisocyanate areas provided they have been informed of the potential risk and have assured the Company representative responsible that, to their knowledge, they do not suffer from any of the above health problems.

.....

Statement to be signed by the visitor

I have read and understood the above information.

To the best of my knowledge I do not suffer from any of the respiratory complaints detailed above.

NAME..... (BLOCK CAPITALS)

SIGNATURE..... DATE.....

Note to personnel accompanying visitors: it is important that one copy of this form be retained by the visitor and another be retained in Company files.

Contractors and technical service personnel may visit sites using MDI and TDI on an intermittent basis only. They need special consideration since their work may lead them into over-exposure situations and they may be working in isolation. Consideration should be given to off-site and/or on-site training of contractors and technical service staff to ensure that they fully understand the health consequences of over-exposure. Long-term contractors should operate within the framework of a company's safety system.

Emergencies in the workplace

All personnel must be capable of responding immediately to an emergency situation. Emergency equipment should be available close to the work station and should include machine stop buttons, and alarms, as well as personal protection. The site needs to have emergency breathing equipment (self-contained equipment with compressed air cylinders or air line equipment and a sufficient provision of air line connections in the workplace). Eye-wash equipment, safety showers, a first aid box and decontamination equipment are required. As emergency showers will be used very infrequently, their operation should be checked at intervals. External showers, for example at unloading areas, should be designed so that they do not freeze in cold conditions. Showers should provide warm water (say at 20 °C) to prevent TDI solidifying if the water is too cold. One or more of the staff in the location should be trained in first

aid techniques and should know how to summon professional help should this ever be required. All staff located in areas where diisocyanates are used should receive training, and refresher training, on first aid procedure specific to diisocyanates. Further discussion of how to deal with emergency situations is to be found in *Key Theme 6*.

All the emergency procedures, including the use of the equipment, must be practised at intervals so that all staff know what to do should an emergency arise. A range of 'routine' emergencies may exist which have preplanned responses. These need preparation and regular training by both workforce and management. The first action in a developing emergency is to stop the process and make it safe, so that remedial action can be started. Once the process has been stopped and emergency ventilation is operating then personnel have time to assess the situation and prepare their next actions. The on-site emergency response teams need to be able to call quickly for outside help (medical or fire fighting services).

Similarly, the off-site emergency services should visit the site in advance to familiarize themselves with the layout, location of the facilities and the hazards likely to be encountered. Regular practices, say annually, will often reveal or clarify weaknesses in the theoretical preparations. Typically, they include issues of access, of the time delay before teams can be effectively on site, and of communication.

It is important to liaise closely with the local community to advise local residents of the nature of the operations, releases to atmosphere, and the implications of an emergency, including any audible or visual alarms on the site. There may also be legal requirements for this information to be given to the local community. It is also useful to have prepared at least a general information and advice statement to distribute to the local community and the media if there is an incident.

Safety signs and posters

It is important to communicate safety instructions clearly, and these should be in the languages used by the workforce. Posters that provide useful reminders on the safe handling of MDI and TDI are available from suppliers and several trade associations. Pictorial signs may be valuable or even mandatory. Some signs may be fixed; others will be portable for use in an emergency. The following examples may be useful.

Some examples of safety signs

NO SMOKING

WEAR RESPIRATORY PROTECTION

WEAR GLOVES

SAFETY GLASSES

FIRE FIGHTING EQUIPMENT

ESCAPE ROUTE

FIRE DOOR

EMERGENCY SHOWER

PROTECTIVE CLOTHING

SELF-CONTAINED BREATHING APPARATUS

EYE WASH

AIR LINE POINT

EMERGENCY STOP BUTTON

DO NOT ENTER: CONTAMINATED AREA

FIRST AID INSTRUCTIONS

DECONTAMINATION EQUIPMENT

ONLY AUTHORIZED EMPLOYEES AND VISITORS WEARING AN IDENTIFICATION BADGE ARE ALLOWED TO ENTER

Releases to atmosphere from polyurethane manufacturing sites

The vapour pressures of MDI and TDI are very low, and normal vapour releases to atmosphere from polyurethane manufacturing sites are, typically, at the parts per billion or parts per trillion level. There is little evidence for any significant releases to atmosphere of diisocyanate aerosols from polyurethane manufacture. Any coarse aerosols released from the processes will generally be deposited on exhaust ducting and react, probably to form polyureas. Fine, gas-like aerosols may leave the exhaust stack, but are likely to evaporate during the dispersion of the releases.

Various abatement methods can be used to reduce airborne releases, notably carbon adsorption and water scrubbing. Carbon adsorption is highly effective in removing diisocyanates (and some co-released gases) from exhaust ventilation air. However, it may be desirable to use an aqueous or other scrubbing method to capture certain other co-releases as well as diisocyanate vapour, depending on the process and on local requirements. Further, regulatory and practical aspects of destruction or cleaning of abatement media need to be considered in the choice of abatement method.

In this text the terms *release* and *release to atmosphere* have been used for losses from the workplace into the external environment. Such releases are often referred to as emissions, but this term is sometimes used by other authors for releases from equipment into the workplace. The term *concentration ex stack* is sometimes used. This relates to the concentration of a chemical just before the exhaust stream emerges from the stack. The term *fugitive emission*

Some authors use the logical combination of *immissions* (into the workplace) and *emissions* (out of the workplace), following German usage.

is commonly used only for losses of a chemical into the workplace, from equipment, spillage, or leakage from equipment. Routine production releases to atmosphere, usually at low concentrations, are sometimes referred to as *normal discharges*.

Only releases to atmosphere are dealt with in this text because releasing MDI or TDI into water or soil under normal operations is unacceptable. Deposition of MDI or TDI to water or soil in accidents within the factory site (that is, within the fenceline) is unlikely to lead to releases beyond the fenceline because of the chemical and physical properties of MDI or TDI: such incidents are covered in *Part 4, The environment*. Normal releases to atmosphere must be considered in terms of potential impact on the environment and on the health of the community beyond the site, that is, beyond the fenceline. Such potential impacts are discussed in *Part 5.6*. This text concerns the sources of airborne releases of MDI or TDI, techniques of abatement and typical concentrations before and after abatement. Details of the methods of sampling and analysis of releases to atmosphere are given in *Part 5.7*.

Properties of MDI and TDI relevant to releases to atmosphere

MDI and TDI have very low volatilities, and hence very low saturated vapour concentrations (SVCs) at the temperatures used in polyurethane processing. The maximum concentrations of MDI and TDI as vapour at different air temperatures are given in Tables 5.4.6, 5.4.7 and 5.4.14. At 20 °C, the SVC of polymeric MDI is 0.03 mg/m³ and of TDI 100 mg/m³: these values apply to equilibrium conditions such as are found only in closed containers. Under the highly nonequilibrium conditions of forced venting, their vapour concentrations are considerably lower than their SVCs, as will be illustrated. Modified MDIs or TDIs are even less volatile than their parent monomers, so will be released from polyurethane processes at even lower concentrations. MDI and TDI vapours adhere strongly to surfaces and there is evidence of adsorption onto ventilation ducts. The high level of adsorptivity of MDI and TDI onto carbon is very well established.

In some processes MDI, and possibly also TDI, may be released as aerosols: these may be reacting polyurethane mix aerosols or diisocyanate deposited onto particulates such as wood dust, for example from particle board production, or fine condensation aerosols of MDI. The aerosols formed from a reacting mix, or from diisocyanate deposited on natural products such as wood dust, are likely to contain predominantly large particles and to be self-neutralizing, due to the presence of polyols or water in the reacting mix and due to water in the natural products, respectively. Such aerosols are likely to be deposited onto ventilation ducting as a result of inevitable air turbulence in extraction systems. Only fine (gas-like) aerosols are likely to escape from the stack to the atmosphere. Vapour released from ventilation ducts will be broken down quickly to common air constituents, due to hydroxyl radical attack in the atmosphere: the tropospheric half-lives of MDI and TDI are of the order of 1 day. Accordingly, there is no long-term cumulative MDI or TDI burden in the environment (see *Part 4, The environment*).

Releases from polyurethane processes

Polyurethane processes differ very considerably in the concentrations of diisocyanates emitted from the equipment. An important consideration is whether there is a need to install a forced air exhaust ventilation system in association with the given equipment. In some processes, the concentrations emitted into the workplace may be well below occupational hygiene limits or even undetectable. Decisions on the need for forced exhaust ventilation stacks to remove diisocyanates from the workplace will depend upon the concentrations of diisocyanates and of other chemicals emitted from processes (co-releases), and upon local regulations. In some cases, particularly in MDI-based processes, the dilution ventilation (normal circulation and replacement of factory air) is adequate to fulfil regulatory requirements. In others, such as in flexible foam slabstock production using TDI, the use of forced exhaust ventilation (local ventilation) is essential to maintain acceptably low workplace concentrations of diisocyanates.

When required, measurements of concentrations should be taken in the ducting of the exhaust system, or near to the top of the stack, but not outside the stack because here the air volume flow rate cannot be measured. Clearly, measurements both in the primary ducting and close to the top of the stack are needed to allow the effectiveness of abatement techniques to be assessed. In some cases the stack will be fed from a plenum drawing air from a number of processing units or work areas: in such cases it may be necessary to make a survey of flow rates and mass balances under different process exhaust conditions to allow meaningful diisocyanate release determinations to be made. It should be noted that exhaust air in ducts may be moving at high speed, probably with turbulent flow. If the diisocyanate is present as vapour only, the process of sampling of exhaust air is not critical and can be nonisokinetic. However, if the diisocyanate aerosols are not gaslike, sampling must be isokinetic (see Part 5.7, *Sampling and analysis*), otherwise results may be meaningless.

Forced ventilation is not usually feasible when the polyurethane processing is not within a factory or when very large objects are being sprayed. Examples of such processes are the spraying of insulation on construction sites, the laying of sports tracks and isocyanate-based paint spraying, including aircraft spraying. In these cases the impact of the operation on the environment and community need to be assessed and precautions taken to reduce the risk to an acceptable level.

Over the past decade there has been a significant increase in interest in releases from stacks, with a corresponding increase in the number of ex stack measurements taken of a wide range of chemical species, including MDI and TDI. Most of these release data have been generated on a single company or single site basis, with the results often submitted to regulators, but not published. To supplement this increased activity, and to allow the development of a dialogue between industry and regulators regarding methodology and release levels, the International Isocyanate Institute Inc. (III) undertook a multi-part project to characterize the releases from various types of MDI- or TDI-based processes, and obtain a profile of the emissions situation in Europe. The project focused on those applications known to use the largest quantities of MDI and TDI, and the effect of abatement was studied. The study also included the measurement of co-releases associated with the given processes and the effect of

References on exposure from outdoor applications and spraying operations

Peterson *et al.* (1962);
Fitzpatrick *et al.* (1964);
Hosein and Farkas (1981);
Bilan *et al.* (1989); Crespo and Galán (1999); Alcares and Reisdorf (1999); England *et al.* (1999); Santolaya *et al.* (2000).

abatement media on their concentrations to allow a comprehensive approach to abatement. The same type of equipment was used throughout, as far as possible, and the studies were undertaken with rigour. For example, analytical equipment was calibrated with samples of the same materials as were used in the factories being tested and, typically, this entailed up to 100 man hours of laboratory work prior to any given factory visit. Where information has been made available, the results have been expressed in one of the following three ways:

1. Concentration of the release

Example: 0.1 mg/m^3 of TDI. The concentration is pertinent to potential respiratory effects in the community. Concentration is used as a regulatory criterion in the EU.

Example: $0.05 \text{ mg NCO group/m}^3$. Concentration may also be expressed in terms of total reactive isocyanate group (TRIG) concentration, a parameter used by some regulators. The TRIG concept is dealt with in detail in *Part 5.6*.

Example: 4 ppb TDI . The parameter used here is *volume in volume*. This measure can be used only for vapour phase concentrations and not for aerosols. See *Part 5.6*.

2. Rate of mass release

Example: $30 \text{ g MDI released per annum}$. Rate of mass loss is a starting point in considering the total environmental burden of diisocyanate. This is a criterion subject to regulatory scrutiny in the US.

3. Percentage of diisocyanate released

Example: $5 \text{ mg MDI released per tonne of MDI processed}$. Percentage loss is a parameter to be considered in judging the efficiency of the combined polyurethane process and abatement system.

Releases from MDI-based processes (except flexible foam)

Almost all rigid polyurethane foam is produced using polymeric MDI. Releases from rigid foam processes vary considerably, depending upon the specific technology used. The lowest levels of releases arise from reaction injection moulding (RIM) techniques in which the mixing head is an integral part of the mould, and the only escape of reacting MDI is from the mould breather holes.

Releases from rigid foam: slabstock and boardstock plants

In the III series of studies on major MDI-using processes (Maddison and Vangronsveld, 2000; Chapman, 2001) releases were measured in the stacks of five factories using two continuous processes: rigid foam slabstock and rigid foam boardstock (lamination) processes. The boardstock processes used flexible facings. The results given in Table 2.11 record the MDI concentration in the stack and the average annual percentage loss of MDI based on MDI throughput, as calculated from the annual output of polyurethane.

The five plants were of different types, situated in five countries and which used different chemical systems based on polymeric MDI. The concentrations of MDI were measured using different analytical methods, which gave

Table 2.11 Summary of MDI releases from five different plants in Europe.

| Process | Stack concentration | Annual MDI mass release | Estimated PUR annual output | | MDI released as % of MDI used |
|--|------------------------|----------------------------|--------------------------------|-------|----------------------------------|
| | μg/m³ | | g | tonne | |
| Continuous boardstock (flexible facings) | | | | | |
| Plant 1 | 1.5 | 76 | 3000 | 6.6 | 4×10^{-6} |
| Plant 2 | 1.3 | 8 | 6800 | 15.0 | 2×10^{-7} |
| Plant 3 | <0.4 | <1 | 1200 | 2.7 | $<1 \times 10^{-7}$ |
| Continuous rigid foam block | | | | | |
| Plant 4 | 3.7 | 23 | 3500 | 7.7 | 1×10^{-6} |
| Plant 5 | 1.6 | 18 | 6000 | 13.2 | 6×10^{-7} |

Conversion factors: 1 g = 0.0022 lb; 1 tonne = 1000 kg = 2205 lb.

For MDI vapour: $1 \mu\text{g}/\text{m}^3 = 0.096 \text{ ppb} = 0.34 \mu\text{g}/\text{m}^3$ NCO group.

extremely similar results on any given plant. The detection limit was about $0.4 \mu\text{g}/\text{m}^3$.

The results showed that releases were at extremely low concentrations (<0.4 to $3.7 \mu\text{g}/\text{m}^3$), such that abatement of these releases was not needed. Annual losses from the plants were calculated as <1 to 76 g, and annual percentage losses were 10^{-6} to $<10^{-7} \%$, corresponding to an average of about 1 to 10 mg/tonne MDI used in the continuous rigid foam block plants. One interesting aspect of the studies on boardstock machines was that all the isocyanate was present as vapour in the releases from the liquid laydown of freshly mixed components, whereas it was all present as particulate at the end of the line where the board was cut off. This indicated that the isocyanate group was associated with partially reacted MDI in the dust from the sawing operation.

Acton (2001) measured releases from a plant producing polyurethane panels with metal facings. Measurements were of concentrations of total reactive isocyanate group (TRIG), VOCs, and toluene, specifically. Two stacks were involved, these relating to releases from the reacting mix lay-down area, and to the panel saw-off area. In Table 2.12 are given the results as MDI concentrations calculated from the TRIG concentrations reported. Concentrations of MDI from the saw-off area were below the level of detection of the HPLC method used. No abatement was needed, even the higher releases from the lay-down area being very considerably lower than the maximum regulated release concentration limit.

Table 2.12 Releases of MDI from a rigid-faced polyurethane panel plant.

| From lay-down area | | | From saw-off area | | |
|---|------------------------------|-------------------------------|---|------------------------------|-------------------------------|
| MDI stack concentration mg/m^3 | Annual MDI mass release g | MDI released as % of MDI used | MDI stack concentration mg/m^3 | Annual MDI mass release g | MDI released as % of MDI used |
| 0.038 | 300 | 4.0×10^{-5} | <0.01 | <10 | $<3.0 \times 10^{-7}$ |
| 0.048 | 56 | 5.0×10^{-5} | <0.01 | <1 | $<3.0 \times 10^{-7}$ |

Releases from fibreboard plants

Maddison and Merckx (1996) have reported on releases from medium density fibreboard (MDF) plants based in three European countries. Fibreboard is produced by coating wood fibres with polymeric MDI, then pressing and heating them in a continuous process. Samples were taken from the exhaust air in stacks from three different points in the fibreboard process. Table 2.13 gives the values recorded, as well as the local regulatory release limits, as then applied. The concentrations ex stack were so low that abatement was not needed.

Table 2.13 Releases from four fibreboard plants.

| Exhaust air from | Plant 1 mg/m ³ | Plant 2 mg/m ³ | Plant 3 mg/m ³ | Plant 4 mg/m ³ |
|------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| Dryer | – | 0.13 | 1.32 | 0.096 |
| Press | 0.045 | 0.87 | 0.09 | 0.045 |
| Wet scrubber | 0.072 | – | – | – |
| Local limit | 0.20 | 5.0 | 5.0 | 0.20 |

Releases from an oriented strand board plant

Oriented strand board (OSB) is produced by continuously coating natural fibres with polymeric MDI, compressing the resulting product and steaming to cure the board. A study was made of MDI releases from the batch press vent of a given process, this being the vent associated with the application and curing of the MDI. The study was of the concentrations in the vent, as measured by two methods, the EPA Draft Method 207, which is very cumbersome, and the OSHA Method 47. The following (Table 2.14) are the summarized results (Karoly, 2001, personal communication):

Table 2.14 Releases (unabated) from an OSB plant.

| EPA Draft Method 207 | mg/m ³ | OSHA Method 47 | mg/m ³ |
|----------------------|-------------------|--------------------|-------------------|
| Range 0.16 to 0.38 | | Range 0.15 to 0.29 | |

Releases from US sites using MDI

A further programme of measurements and calculations was carried out by the US Chemical Manufacturers Association, its successor organization, the American Chemistry Council, the Alliance for the Polyurethanes Industry and the USEPA. The aim of this programme was quite different from that of the above studies, in that an attempt was made to estimate the maximum annual mass of MDI liberated to the atmosphere in the US, irrespective of ex stack concentration or percentage loss of MDI during processing. This work was to support a submission to the USEPA that there was no plausible case for listing MDI as a *High Priority Urban Air Toxic* and to develop a more accurate National Toxics Inventory for MDI (Price *et al.*, 1998). Results taken from that survey are given in Table 2.15. It should be emphasized that the values were

worst case calculations for sites releasing the maximum masses of MDI per annum for the cited applicational category. Thus, they should not be interpreted either as typical, or as related to a single *process*. However, they are reproduced here to give an insight into the order of maximum losses from US sites. A review of the US situation regarding MDI releases from 1088 sites is given by Robert *et al.* (2001). Miller (2001) has reviewed measured MDI releases from foundries in the US.

Table 2.15 Estimated maximum annual releases of MDI from selected US sites.

| Category | Estimated releases | | Category | Estimated releases | |
|-----------------------------|--------------------|---------|----------------------|--------------------|---------|
| | kg/year | lb/year | | kg/year | lb/year |
| Air filter | 3 | 7 | Foam production | 10 | 22 |
| Appliance | 10 | 22 | Foundry castings | 6 | 13 |
| Appliance (truck) | 2 | 5 | Laminating | 6 | 13 |
| Automotive | 3 | 7 | Mobile home products | 4 | 10 |
| Boat building | 0.5 | 1 | Oil | 0.5 | 1 |
| Coating (adhesive) | 3 | 7 | Packaging | 3 | 7 |
| Coating (elastomers) | 3 | 7 | Rebonding | 4 | 9 |
| Coating (sealant) | 3 | 7 | Recreation | 3 | 7 |
| Coating (thermoplastic PUR) | 3 | 7 | Shoe soling | 3 | 7 |
| Custom moulding | 0.5 | 1 | Fibres | 3 | 7 |
| Door production | 1 | 3 | Specialty production | 4 | 10 |
| Electronics | 3 | 7 | Tyre filling | 1 | 3 |
| Filter devices | 0.5 | 1 | Water heaters | 3 | 7 |

Releases of MDI and TDI from flexible foam moulding processes

Flexible foam moulding is an operation whereby a polyurethane reacting mix based on TDI, MDI or mixed MDI and TDI, or derivatives of them, is poured or injected into a mould. The mould is opened when the foam has cured long enough to allow damage-free handling. In the traditional moulding systems (typically using TDI) the residence time in the mould is reduced by passing the moulding through an oven: these are hot cure processes. With some systems (typically using MDI) no oven is required: these are cold cure processes. In an III study in three European countries (Table 2.16) (Maddison and Vangronsveld, 1996; Chapman, 2001) measurements were taken in the stacks of five flexible foam moulding lines manufacturing automotive seats. The stacks were not fitted with abatement equipment. The results of measurements in the above study on other released species, such as catalysts and other chemicals used in production, are given by Maddison and Vangronsveld (1996).

Releases from flexible foam slabstock production using TDI

In this process the reacting polyurethane liquid mixture is poured into a moving trough in a tunnel which is equipped with exhaust ventilation. The mixture reacts to form a continuous block of foam, typically about 1 m × 2 m

Table 2.16 Summary of releases (unabated) from flexible foam moulding processes.

| Factory | Process | Stack concentration | | Annual release rate | | Estimated PUR annual output | | Diisocyanate released as % of diisocyanate used | |
|---------|-------------------|--------------------------|--------------------------|---------------------|----------|-----------------------------|------------|---|--------------------|
| | | MDI mg/m ³ | TDI mg/m ³ | MDI g | TDI g | tonne | million lb | MDI % | TDI % |
| 1 | Car seating | | | | | | | | |
| | cold cure | <0.0001 | 0.019 | } 26 | 1760 | 1400 | 3.1 | 2×10^{-5} | 6×10^{-4} |
| | cold cure | <0.0001 | 0.007 | | | | | | |
| | cold cure | 0.0005 | 0.004 | | | | | | |
| 2 | Car seat moulding | | | | | | | | |
| | cold cure | 0.0125 | – | 794 | – | 420 | 0.9 | 6×10^{-4} | – |
| | Headrest moulding | | | | | | | | |
| | cold cure | 0.0009 | – | 75 | – | 250 | 0.6 | 9×10^{-5} | – |
| 3 | Moulding | | | | | | | | |
| | cold cure | <0.0001 | – | <2 | – | – | – | – | – |
| | hot cure | – | 0.5 | } – | 13 620 | 510 | 1.1 | – | 9×10^{-3} |
| | hot cure | – | 0.38 | | | | | | |

Conversion factors:

MDI vapour, 1 mg/m³ \equiv 0.096 ppm;
TDI vapour, 1 mg/m³ \equiv 0.14 ppm;1 g = 0.0022 lb; 1 tonne = 1000 kg = 2205 lb;
1 short ton (US) = 907 kg = 2000 lb.

cross-section. Lengths of block are sawn off and stored in a vented storage area for about 1 day to allow the polymerization reaction to come to completion and for blocks to cool.

Over the past 20 years many programmes of work have been carried out to measure the concentration of TDI releases from flexible foam slabstock production. These have focused on concentrations in exhaust stacks, but some practical studies have yielded information on environmental concentrations. Tu and Fetsch (1980) reported average levels from 3 to 8 mg/m³ (400 to 1100 ppb) from a range of 0.1 to 33.5 mg/m³ after a survey of stack concentrations of a number of foam plants. Grey and Chadwick (1979) reported inlet concentrations to an alkali scrubber between 300 and 670 ppb. The use of modern side and top paper technology on foam slabstock processes has been widely adopted since some of the early measurements were made, and from more recent measurements in the ducting of three plants, maxima around 300 ppb TDI are now common at air flow rates above 40 000 m³/h.

In Table 2.17 is given a summary of results obtained in III studies (Glover and Maddison, 1994; Vangronsveld and Maddison, 2002). The

Some of the factors influencing TDI release concentrations are as follows:

Foam system variables:

- isocyanate index;
- foam density;
- cell opening characteristics.

Plant design/geometry

Processing factors:

- laydown conditions;
- edge papers;
- top papers.

Ventilation air throughput

values in this table were measured pre-abatement. The post-abatement values for all factories are given in Table 2.28.

In Table 2.18 are given the ranges of concentration recorded by the cited authors in the exhaust stacks of flexible foam slabstock plants, pre-abatement. The concentration results

are in a rather narrow range and are valuable in that regulators can make estimates of levels of release, and from these estimate community exposure.

Table 2.17 TDI release concentrations (pre-abatement) from flexible foam slabstock machines.

| Factory | Foam type | TDI concentration | |
|---------|-------------------------------------|-------------------|------|
| | | mg/m ³ | ppb |
| 1 | Standard polyester | 0.49 | 0.07 |
| 2 | Standard polyether | 5.9 | 0.83 |
| 2 | High resilience polyether | 1.9 | 0.27 |
| 3 | Standard polyether | 1.26 | 0.18 |
| 3 | Combustion modified high resilience | 0.15 | 0.02 |
| 4 | Polyether, carbon dioxide blown | 0.8 | 0.12 |

Table 2.18 Ranges of TDI emissions from flexible foam slabstock processes (pre-abatement).

| Concentration | | Mass released per quantity of TDI processed | | Reference |
|---------------|-------------------|---|----------------------|--------------------------|
| ppm | mg/m ³ | g/tonne ^a | % | |
| 0.3 to 0.7 | 2 to 5 | – | – | Grey and Chadwick (1979) |
| 0.4 to 1.1 | 3 to 8 | 50 | 5×10^{-3} | Tu and Fetsch (1980) |
| 0.02 to 0.85 | 0.15 to 5.9 | 25 | 2.5×10^{-3} | III studies: Table 2.17 |
| 0.2 to 0.5 | 1 to 4 | – | – | Palfy (2000/2001) |

Conversion factors: 1 tonne = 1000 kg = 2205 lb; 1 g = 0.0022 lb; 1 short ton (US) = 907 kg = 2000 lb.

^aFor comparison, the losses of MDI from rigid foam slabstock were in the range of 1 to 10 mg/tonne. See Table 2.11.

However, the concentration results should be considered with some caution. Firstly, they are highly dependent upon air flow rate and ducting arrangements, and these are specific to a given situation. Secondly, they depend upon the specific production process used. In summary, *concentration is specific to site and process and 'typical' or average values cannot be obtained from Table 2.18*. A specific situation can be characterized only by direct measurement of concentration.

Metcalf and Sweet (1993) attempted to devise a formula to calculate the concentrations of releases from flexible foam slabstock plants. The formula was derived from the results of measurements on several US plants, and gave a good statistical fit. However, when the results from the III studies cited above were applied, the formula gave the correct value in only one case. The formula is probably applicable only to processes which are very similar to those used to derive the formula.

TDI isomer ratios in releases from flexible foam slabstock processes

It has been well established that TDI isomer ratios change during polyurethane flexible foam processing. The airborne TDI released from the process is richer in 2,6-TDI than is the original TDI (Nutt *et al.*, 1979). This is mainly attributable to the faster rate of reaction of the 2,4-TDI isomer with the reaction mix. It has also been shown that the percentage of 2,6-TDI in the air above a flexible foam line increased along the line, as compared with 2,4-TDI. In

References to change in isomer ratio during polyurethane processing
 Grey and Chadwick (1979);
 Nutt *et al.* (1979); Rando
 and Hammad (1985);
 Tinneberg *et al.* (1997).

Table 2.19 are given ratios calculated from the results of measurements of individual TDI isomers in flexible foam slabstock and moulding operations:

Table 2.19 Change in TDI isomer ratio from that in the original 80/20 TDI.

| Plant | Type of foam | 2,4-TDI in raw material % | 2,4-TDI in TDI in exhaust stream % |
|--|----------------------------------|------------------------------|---------------------------------------|
| Slabstock production | | | |
| 1 ^a | Standard polyester (TDI) | 80 | 27 |
| 2 ^a | Standard polyether (TDI) | 80 | 20 |
| 3 ^b | Standard polyether (TDI) | 80 | 39 |
| 4 ^b | Standard polyether (TDI) | 80 | 41 |
| 5 ^b | Standard polyether (TDI) | 80 | 47 |
| 6 ^a | Fire retarded high modulus (TDI) | 80 | 26 |
| 7 ^a | Combustion modified (TDI) | 80 | 32 |
| 8 ^c | Polyether, carbon dioxide blown | 80 | 19 |
| Moulding production^d | | | |
| 8 | Cold cure (MDI/TDI) | 80 | 50 |
| 9 | Cold cure (MDI/TDI) | 80 | 21 |
| 10 | Hot cure (TDI) | 80 | 33 |
| 11 | Hot cure (TDI) | 80 | 37 |

^aGlover and Maddison (1994).

^bNutt *et al.* (1979).

^cVangronsveld (2001).

^dMaddison and Vangronsveld (1996).

Releases from flame lamination processes

Flame lamination is a technique whereby a thin layer of polyurethane flexible foam is combined with a textile or textiles to produce a fabric with different properties. The process involves heating a continuous thin layer of polyester or polyether foam with a bank of flames. The melted surface of the foam is self-adhesive and bonds to the textile in the combining process. The exhaust stack gases comprise low concentrations of diisocyanates and combustion gases such as carbon monoxide, carbon dioxide and nitrogen-based compounds. In Table 2.20 are given the results of measurements taken of diisocyanates in the gases in the stack (Glover and Maddison, 2000) prior to carbon abatement. Their report also gives information on the concentrations of other chemicals in the exhaust stream, before and after abatement: data on the abatement of TDI are given in Table 2.28.

Releases from hot-wire cutting of flexible foam

In Table 2.21 are given the concentrations of TDI measured by Nutt (1982) in the exhaust gases from hot wire cutting of fire-retarded polyether slabstock foam. The HPLC traces indicated that a diversity of isocyanate-ended species might also be present. Interestingly, the change of isomer ratio of the TDI

Table 2.20 Stack concentrations of diisocyanates from flexible foam flame lamination processes (pre-abatement).

| Foam type | Diisocyanate concentration mg/m ³ | | |
|-------------------------------|--|---------|----------|
| | 2,4-TDI | 2,6-TDI | 4,4'-MDI |
| Standard polyester foam (TDI) | 0.30 | 0.05 | – |
| Standard polyether foam (TDI) | 2.00 | 0.22 | – |
| Standard polyether foam (MDI) | – | – | 0.048 |

Conversion factors: MDI vapour, 1 mg/m³ \equiv 0.096 ppm;
 TDI vapour, 1 mg/m³ \equiv 0.14 ppm.

Table 2.21 Concentrations of TDI in hot wire cutting exhaust gases.

| Test | 2,4-TDI mg/m ³ | 2,6-TDI mg/m ³ | TDI total mg/m ³ | 2,4-TDI in TDI in exhaust stream % |
|------|------------------------------|------------------------------|--------------------------------|--|
| 1 | 1.0 | 2.9 | 3.9 | 26 |
| 2 | 1.1 | 2.2 | 3.3 | 33 |
| 3 | 2.1 | 3.7 | 5.8 | 36 |

Conversion factor: TDI vapour, 1 mg/m³ \equiv 0.14 ppm.

from that of 80 % 2,4-TDI in the original material to those in the exhaust air samples indicates preferential thermolysis of the polyurethane bond formed from the polyol and 2,6-TDI. Whilst the precision of these figures is lower than those normally achieved in recent studies, and the results represent only one scenario, the broad indications of this work are useful, given that hot wire cutting is still used.

Releases of MDI and TDI from prepolymer and manufacturing elastomer processes

MDI releases from the production of an MDI prepolymer, and its use in elastomer manufacture have been studied (III unpublished data). Measurements were taken (1) during charging of the prepolymer reaction vessel and (2) from the reaction vessel for producing about 10 tonne of prepolymer. The prepolymer was used for producing elastomer shoe soles by (3) dispensing the prepolymer/polyol blend from a mixing head into moulds. Subsequently, the soles

Table 2.22 Prepolymer and shoe sole manufacture: MDI release concentrations.

| (1) Charging $\mu\text{g}/\text{m}^3$ | (2) Prepolymer manufacture $\mu\text{g}/\text{m}^3$ | (3) Moulding $\mu\text{g}/\text{m}^3$ | (4) Degreasing $\mu\text{g}/\text{m}^3$ |
|--|---|--|--|
| <1 | <1 | <1 | <1 |

Detection limit: 1 $\mu\text{g}/\text{m}^3$ for MDI.

were (4) degreased and finished. The results are given in Table 2.22. A limited survey of a few elastomer production units suggests that releases of MDI and TDI are very low, that is, of the order of $0.3 \mu\text{g}/\text{m}^3$ or even lower (Hurd, 1995, personal communication).

Releases of compounds other than MDI or TDI from polyurethane processes

Although this text is concerned primarily with MDI and TDI, releases of other chemicals present in polyurethane processing need to be considered, in order to assess what method or methods of abatement are appropriate, if any. Chemicals which are co-released include auxiliary chemicals used

in polyurethane processes, such as catalysts, blowing agents, antioxidants and solvents present in some raw materials, as well as solvents from mould release agents or from solvent flushing of mixing heads. It may be necessary to consider such chemicals within regulations on *volatile organic compounds* (VOCs), as well as on specific species.

For instance, in the screening tests for the research project discussed later, the following compounds were measured in the releases from the stack of a flexible foam slabstock

Volatile organic compounds

VOCs have become an issue within the context of global warming. Destruction of the ozone layer is believed to be a function of both type and concentration of certain VOCs. Definitions of VOCs differ very significantly according to regulatory authority and these definitions are not scientifically compatible. TDI, and especially MDI, might be considered by the scientist as *involatile* organic compounds (see Tables 5.4.7 and 5.4.14). However, both MDI and TDI were listed as VOCs within the terms of the USEPA definition (USEPA, 1994) which is: *VOC means any compound of carbon, excluding CO, CO₂, H₂CO₃, metallic carbides or carbonates, and (NH₄)₂CO₃, that participates in atmospheric photochemical reactions.* Certain solvents are exempted because of their photochemical reactivity. The European Union definition, based on volatility, excludes MDI and TDI.

process (Maddison and Vangronsveld, 1996):

- methylene chloride;
- silicone carrier solvents;
- toluene;
- tertiary amine catalysts.

The same research programme has given valuable quantitative data on such substances released from several types of polyurethane production. These data will allow an assessment of the risks that the substances may constitute and what effective technical and economic abatement technology it may be necessary to consider.

Tertiary amine catalysts

Gas chromatography with mass spectrometry has been used to measure the concentrations of some typical tertiary amine catalysts released from polyurethane processes producing several types of polyether and polyester flexible foam slabstock and mouldings. The total concentration determined in the releases was not more than 1 ppm from each of the three polyether foam production plants and 6.5 ppm from a polyester foam production line. The data suggest that a minor percentage of the tertiary amine catalyst used in the reaction mix is emitted in the foam conveyor section of the process, the rest being lost in cure and storage areas, or retained in the foam. Catalyst manufacturers are

offering wider ranges of reactive catalysts, and polyol-grafted catalysts, further to reduce releases to atmosphere.

Blowing agents

Blowing agents currently used in polyurethane technology include liquid carbon dioxide, isopentane, cyclopentane, butane, propane, acetone and the fluorocarbons containing hydrogen, such as HCFC 141B, HFC 152A, HFC 134A and HFC 245FA. A number of analyses of the release concentrations of CFC-11, a chlorofluorocarbon, and methylene chloride, both of which were used very widely in flexible foam processes, have been reported, as have assessments of the percentage recovery of the CFC-11 by the use of activated carbon beds (Sporon-Fiedler, 1986; Nutt and Skidmore, 1987). Although these two substances are being phased out as blowing agents, the results are useful in understanding releases of other blowing agents in what is essentially an unchanged process. The concentrations in releases of the blowing agent methylene chloride have been measured and pre-abatement concentrations up to 24 g/m³ have been found, similar to the levels of CFC-11 reported. With both CFC-11 and methylene chloride, approximately 50 % of the total used is emitted in the conveyor section of the flexible slabstock process.

Abatement of releases

Criteria for abatement

There was little regulatory interest in releases of MDI or TDI until the mid 1990s. This was primarily because of the low levels of releases: also, there had been little regulatory activity associated with chemicals, in general. Further, it had been well established (*Part 4, The environment*) that MDI and TDI have little environmental impact and that they decay in air. However, several regulatory authorities have now established ex stack maximum release concentrations for these materials. Further, in the US there are fenceline (community) maximum concentrations for MDI and TDI, within the IRIS programme of establishing community risk from releases of chemicals.

Ex stack concentrations are relatively easy to determine, using well-established methods. Fenceline compliance measurements are more complex: they involve direct measurements at the limits of analytical methodology (typically 1 to 100 parts per trillion), or the use of modelling of ex stack concentrations. Modelling involves the use of meteorological conditions at the site, factory site parameters and geographical features of the surrounding area. These topics are discussed in *Parts 4* and *5.6*.

Abatement methods

Several methods have been investigated to reduce releases of MDI or TDI present in the exhaust air of ventilation stacks. Of the methods tested, only neutral and alkali aqueous scrubbing and carbon adsorption methods have proved to be both practically and economically viable. The choice of method depends upon the co-releases of chemicals which also have to be abated. Pilot studies have been carried out on the destruction of releases using OH radicals or biological media but these have not led to commercial development of

the methods, probably due to the simplicity and effectiveness of carbon or aqueous systems.

Activated carbon adsorption systems

Design of activated carbon units

A wide range of designs has been tested, and selected ones used commercially, over the past 25 years. The carbon has been used as plates or in granular form. Whilst carbon in the plate form avoids the problem of air channels forming, the problems of sealing the plates in the exhaust ducting have been found to be significant. Carbon, as granules, has been used in systems with multiple layers, or as a single large bank. A problem with multiple layers is to prevent extensive channelling (and hence short contact time of the carbon with the exhaust gases) at each layer. Modern systems use large banks of granular carbon either in a cylinder or in an annular configuration (see Figure 2.39).

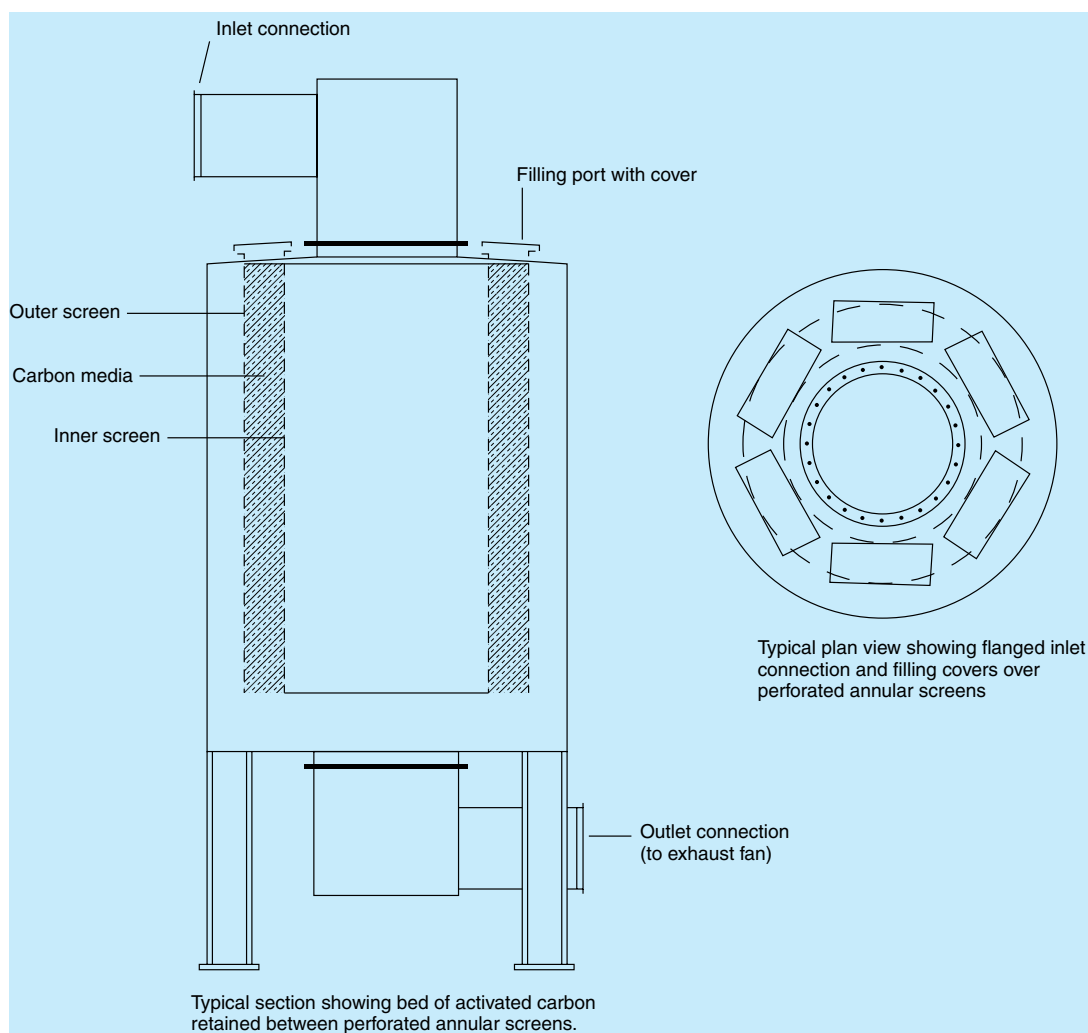


Figure 2.39 Diagram of the operation of an annular carbon bed abatement unit. Reproduced by kind permission of Camfil, Blackburn, UK

There are five critical aspects to be considered:

- contact time of MDI or TDI with the carbon;
- type of carbon;
- channelling in the carbon bed;
- clogging of the carbon bed;
- blocking of the carbon by debris.

The *contact time* of the exhaust air with the carbon is defined as the velocity of air flow through the bed divided by the bed thickness: for example, a linear velocity of 0.4 m/s (1.3 ft/s) and a bed thickness of 1 m (3.3 ft) would give a contact time of 2.5 s. Control of linear velocity, and hence residence time, of the exhaust gases in the adsorption unit is critical. For effective TDI removal one manufacturer has recommended that the air velocity should not exceed 0.5 m/s (1.6 ft/s) and that the contact time should be at least 2 s. Adsorbers using these criteria have operated successfully for over 15 years, reducing TDI emissions to acceptable discharge concentrations.

Since beds may use several tonnes of carbon and last for years, the choice of *carbon type* is critical. It is important that experts be consulted and, if necessary, small-scale laboratory tests carried out. It is not difficult to calculate the required contact time. However, in that respect it should not be assumed that there is even flow through the carbon. *Channelling in the carbon bed*, which results in air passing preferentially through open channels formed mechanically in the carbon bed, leads to reduced contact time of the exhaust gases with the carbon, and hence to lower adsorption efficiency. *Clogging of the carbon bed*, where carbon particles adhere to each other at the inlet of the bed to form a mass of low permeability, can also be a problem: the pressure across the bed becomes so high that exhaust gases cannot be forced through it. Mechanical break-up of the carbon at the inlet end of the bed may be necessary to prevent this. An associated phenomenon is *blocking of the carbon* by dust and other debris. Some manufacturers use a so-called *sacrifice layer* before the carbon adsorption unit. This is a unit containing cut scrap flexible polyurethane foam or other removable material. This has the function of reducing channelling of the air by preventing any debris from the air collecting at the inlet of the carbon adsorption unit. Further, it is well known that flexible foam adsorbs diisocyanates very strongly, so the concentration of diisocyanate entering the carbon adsorption unit is already reduced. The sacrifice layer is replaced very frequently at low cost. This use of flexible foam for the abatement of diisocyanate has been described (Wood *et al.*, 1993).

The concentration of TDI decreases as the air passes along ducting to the carbon bed, due to adsorption on the side walls. One company using a substantial length of ducting found a reduction of 30 to 40 % of the initial TDI concentration. Thus, when measuring the efficiency of a scrubber unit the inlet concentration should be measured near to the entrance of the scrubber.

In Figures 2.40 and 2.41 are illustrated carbon adsorption units for flexible foam slabstock releases, and flame lamination releases, respectively. There has been considerable experience with such carbon beds, some of which is described below. In one case, the carbon bed was changed after 7 years of operation, not because of loss of efficiency (still >99 %), but because of the increase in back pressure. The use of a simple acrylic filter impregnated with



Figure 2.40 Carbon abatement unit for emissions from flexible polyurethane foam processing. Reproduced by kind permission of Camfil, Blackburn, UK



Figure 2.41 Carbon abatement unit for emissions from a polyurethane flame lamination process. Reproduced by kind permission of Camfil, Blackburn, UK

activated carbon before the main carbon bed, not only removed particulates, but also reduced the concentration of TDI by approximately 20 %. The acrylic filter needed to be renewed frequently. In another case, the carbon bed was reported as freezing at very low ambient temperatures and it consequently failed to operate until heated by warm air. In Table 2.23 are given the results of analysis of the same type of carbon used in three different carbon adsorbers over a period of 7 years (III unpublished data). It had already been ascertained that the maximum loading of the given carbon was about 25 g per 100 g reaction product calculated as TDI product. It can be seen that there was a gradation of loading from the inlet to the outlet in all three adsorbers. In Adsorber 1 the saturation loading (25.4 g per 100 g carbon) had been reached and the remaining lifetime of this adsorber was very limited because of the reducing carbon contact time: in the cases of Adsorbers 2 and 3 there was still considerable capacity, this being due to the lower concentrations of TDI being passed through them.

Table 2.23 Loadings of TDI/reaction product on carbon adsorbers.

| Position in bed | TDI/reaction product loading on carbon g/100 g | | |
|-------------------|--|------------|------------|
| | Adsorber 1 | Adsorber 2 | Adsorber 3 |
| Exhaust gas entry | 25.4 | 22.8 | 24.0 |
| Middle | 22.3 | 7.3 | 6.0 |
| Exhaust gas exit | 11.8 | 5.1 | 4.1 |

Note: saturation loading by TDI is about 25 g per 100 g carbon.

Analysis of used carbon

Samples of activated carbon from the above three carbon adsorbers were examined. The spent carbon was grey in colour. Analysis of this spent carbon showed that neither TDI nor TDA were detectable (detection limit: 5 mg/kg) so that any nitrogen present would probably be as polyureas. The results of chemical analysis are given in Table 2.24, where the figures are expressed as percentages of the carbon in the bed (w/w). In addition to the results of analysis are given calculated values of the percentage of polyurea which would be formed if all the nitrogen were converted to polyurea: the value approaches that of 25 g per 100 g carbon given in Table 2.23.

Table 2.24 Analysis of carbon from beds.

| Bed | Extractable nitrogen | TDI | TDA | Fixed nitrogen | |
|-----|----------------------|-----|-----|----------------|------------------------|
| | % | % | % | % | % as urea ^a |
| 1 | nd | nd | nd | 4.0 | 21 |
| 2 | nd | nd | nd | 3.2 | 17 |
| 3 | 0.06 | nd | nd | 3.2 | 17 |

nd = not detected (detection limit 5 mg/kg).

^aCalculated.

Reactivation of activated carbon

The above carbon was reactivated by heating in a process used by the original supplier. The results of reactivation tests showed that the grey colour and polymerization products could be totally removed along with the adsorbed impurities. The reactivated product was found to have good adsorption capacity, as measured by benzene adsorption, which is used as a standard. It was concluded that the spent carbon could be reactivated and re-used in air purification applications.

Aqueous scrubbing

Aqueous alkali scrubbing of MDI and TDI has been used with success in the UK for more than 20 years. Typical systems use a bed packed with polypropylene spheres to provide a large surface area for the scrubbing agent, sodium hydroxide solution. The alkali trickles through the bed under gravity, the extract air is forced upwards and permeates the bed, and the diisocyanate is removed by reaction with the alkali. The alkali is recirculated. Grey and Chadwick (1979) published details of the design of the Cleme Gas Scrubber, and reported that a conventional twin impingement plate scrubber unit gave only approximately 50 % efficiency. Modifications were carried out to the design and eventually an efficiency of greater than 90 % was achieved. It should be noted that the concentration of diisocyanate in the gas phase before abatement is so low that there is negligible change of the temperature in the aqueous scrubber due to the heat of reaction.

Grey and Chadwick reported that the first unit installed made no provision for easily monitoring and adjusting the strength of the sodium hydroxide scrubbing liquor. As a result of the removal of carbon dioxide from the exhaust ventilation gas stream, sodium hydroxide became progressively consumed and converted through sodium carbonate to sodium bicarbonate. The scrubbing action of 0.3 to 5 % sodium carbonate solution was known to be as efficient as 0.25 to 4 % sodium hydroxide, but sodium bicarbonate was less effective. Steps were taken to improve the control of alkalinity of the scrubbing medium using an automatic dosing system, which replenished the sodium hydroxide level by injecting 30 % aqueous sodium hydroxide through appropriate valving and pumps. Other designs of aqueous scrubber have been developed. One foam manufacturer evaluated a packed tower design. The work indicated that an efficiency of greater than 95 % using alkali scrubbing could be guaranteed. Efficiencies of the order of only 80 % were achieved when water rather than aqueous alkali was used as the scrubber liquor. A possible improvement to this problem was used by one foam manufacturer, who found that the replacement of alkali by aqueous solutions of urea gave scrubbing efficiencies close to those obtained with alkali, and significantly higher than those with water.

An improvement over water scrubbing might be to combine it with aqueous oxidation. It is already known that MDI and TDI are oxidized by hydroxyl radicals which could be generated in the aqueous system. Pilot trials have indicated that such a system would be viable (Barker and Jones, 1988)

Neutral aqueous scrubbing can be achieved by the use of venturi systems. Hurd (1988) has described the use of single-stage and multi-stage venturi installations on two UK flexible foam slabstock plants. A single venturi

installation on one plant operating at approximately 50 000 ft³/min of air gave about 50 % efficiency with inlet TDI concentrations of around 1000 ppb.

Very good results have been obtained, however, using three venturi scrubbers in series. This plant operated with an air extraction rate of 64 000 ft³/min (115 200 m³/h) of air. The inlet TDI concentration was monitored continuously by a paper tape monitor. The data from the monitor were fed to a microprocessor. Automatically, the number of venturis required to reduce the outlet TDI concentration to below 20 ppb were brought into operation, assuming 55 % efficiency in each successive venturi jet in the series of three jets. The full series of three were required only when particular foam formulations leading to higher levels of TDI emissions were being run. A maximum scrubbing efficiency of not less than 90 % was obtained with all the venturis in operation. Water usage was high, however, so a recirculation system was established.

Effluent from aqueous scrubbers

There are widespread regulations regarding the release of aqueous factory waste into water systems. In order to conform to acceptable standards a knowledge of the composition of the scrubbing liquors, and the local criteria for dilution and disposal, are essential. The effluent waters from two polyurethane factories releasing effluents into water systems were analysed within an III programme (Chapman, 2001).

One of the factories used a water scrubber, whereas the other factory employed an alkali scrubber. TDI could not be detected in either effluent. However, low levels of its reaction product, toluene diamine (TDA), were found in both. TDA is expected to be easily removed from the effluent by a water treatment plant since it is very strongly adsorbed onto the activated sludge (Cowen *et al.*, 1998). Measurements of Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC) and Chemical Oxygen Demand (COD), along with concentrations of various chemical species were reported. The overall conclusion was that upon natural dilution of the effluent, it would have similar characteristics to those of water from public treatment plants. Solids formed in the neutralization process, and removed from the above aqueous effluent, should be disposed of in conformity to local regulations. Whilst there has been a general trend to use carbon abatement rather than the less efficient aqueous systems, interest in aqueous systems continues (Griggs *et al.*, 2000).

Efficiencies of TDI abatement: pilot studies

Urano at Yokohama National University (1978) carried out work on the use of activated carbon to adsorb TDI. He reported that an adsorption capacity of 0.3 to 0.5 g TDI/g carbon would be achievable even at low concentrations of TDI in air. These values should be viewed in the light of those given in Table 2.23. A very high adsorption rate for CFC-11 (which was then used universally as a blowing agent) was also reported. He also reported that for triethylenediamine (TEDA), a widely used polyurethane catalyst, the adsorption capacity of the carbon was large, but the adsorption rate was low (this may have been due to adsorbed TEDA being lost from the carbon to the exhaust stream). An important contribution to the data on the use of activated carbon for TDI removal and CFC recovery was made by Gans *et al.* (1983) and by Sporon-Fiedler (1986).

Gans and his co-workers at Stuttgart University carried out a detailed investigation of the removal of TDI and CFC recovery from polyurethane emissions,

References on

carbon abatement

Urano (1978, 1979); Gans *et al.* (1983); Urano and Yamamoto (1984); Sporon-Fiedler (1986); Nutt and Skidmore (1987).

both on the laboratory scale and on a large scale pilot plant, in collaboration with industry. Further, more detailed analytical tests on this pilot plant were reported by Nutt and Skidmore. They reported that the unit was >99 % efficient for TDI removal and that CFC-11 recovery was also viable.

Efficiency of TDI abatement: large scale experience using activated carbon units

Following the pilot scale tests reported above, a number of carbon adsorbers were installed on flexible polyurethane foam plants, notably in the UK, Holland and Belgium. Data are now available from these units in terms of efficiency, life and the cost per tonne of TDI treated. Two units which had been operating for over 7 years showed no detectable TDI at the exit from the scrubbers. It has been found that a reduction in the air volumes used in polyurethane flexible foam slabstock production was necessary to obtain efficient and economic abatement methods, since capital costs, running costs and space requirement of abatement equipment all increase substantially with increased air volume. Costs will also of course be dependent upon plant output, space requirements and other factors. Substantial reductions of air volumes can be achieved by a study of operating and ventilation conditions. One company, when installing carbon adsorption units, reduced exhaust volumes on a flexible foam slabstock line from approximately 80 000 to 45 000 m³/h using extraction above the side wall instead of the conventional overhead exhaust. In spite of this change, concentrations of TDI in the workplace did not increase.

The results from a later research programme confirmed the efficiency of activated carbon units for TDI removal (see Table 2.25 for example). Running costs vary depending on the variables outlined but, as a general guide, are of the order of US \$2.5 per tonne of TDI processed by the factory (2001).

Table 2.25 The efficiency of carbon bed abatement of TDI from flexible foam production.

| Foam type | TDI concentration before abatement mg/m ³ | TDI concentration after abatement mg/m ³ | Efficiency % |
|-------------------------------|--|---|-----------------|
| Polyester | 0.246 | 0.0058 | 98 |
| Polyether standard | 2.95 | nd ^a (<0.001) | approx. 100 |
| Combustion modified polyether | 0.794 | nd (<0.001) | approx. 100 |

Conversion factor: TDI vapour, 1 mg/m³ \equiv 0.48 mg/m³ NCO group \equiv 0.14 ppm.

^and = not detected.

Abatement of releases from flame lamination

In Table 2.26 are given the effects on concentrations of MDI and TDI releases from flame lamination of MDI-based and TDI-based polyurethane foams of using carbon abatement (Glover and Maddison, 2000). All concentrations of MDI or TDI, post-abatement, were below any regulatory maximum requirement, and below the detection limits of the method, which were 0.03 mg/m³ for MDI and 0.02 mg/m³ for TDI.

The authors also reported on the abatement of carbon dioxide, carbon monoxide, nitrogen oxides, hydrochloric acid and hydrocyanic acid from the exhaust

Table 2.26 The abatement of MDI and TDI from flame lamination processes.

| Foam type | Released species | Concentration pre-abatement mg/m ³ | Concentration post-abatement mg/m ³ | Efficiency of abatement % |
|-----------------|------------------|--|---|------------------------------|
| Polyester (TDI) | 2,4-TDI | 0.31 | <0.02 | >94 |
| | 2,6-TDI | 0.53 | <0.02 | >96 |
| Polyether (TDI) | 2,4-TDI | 2.12 | <0.02 | >99 |
| | 2,6-TDI | 0.24 | <0.02 | >90 |
| Polyether (MDI) | MDI | 0.05 | <0.03 | nm ^a |

^anm = statistically not meaningful to calculate this value.

stream. In most cases gases were reduced to, or near to, the level of the analytical detection limits. This work was carried out using new carbon, so the above values reflect optimal abatement for that plant. However, since that study was completed (in 1993) there have been significant developments in the treatment of carbon to adsorb specified chemicals such as hydrochloric acid, hydrocyanic acid and amines, in the last case using acid-treated carbon.

Abatement of blowing agents, amine catalysts and other species

It is beyond the scope of this text to deal with the abatement of species other than MDI and TDI. Furthermore, individual abatement scenarios need to be examined to allow meaningful approaches to co-abatement to be made. The citations provided below give a considerable amount of information about the concentrations of chemical species which may be released from MDI- or TDI-based processes.

References to studies about diisocyanate co-releases

In these reported studies, co-releases were determined, in most cases before and after abatement.

Flexible foam slabstock

Glover and Maddison (1994)

VOCs, methylene chloride, toluene, amine catalysts, metal catalysts, organophosphorus, halogens, substituted phenols, other.

Vangronsveld (2001)

Fire retardants, blowing agents, glycols, aliphatic amine catalysts, VOCs.

Flexible foam moulding

Maddison and Vangronsveld (1996) and Chapman (2001)

VOCs and tertiary aliphatic amines.

Flame lamination

Glover and Maddison (2000)

Carbon monoxide, carbon dioxide, hydrocyanic acid, hydrogen chloride, nitrogen oxides (NO_x), aromatic amines, VOCs, acid gases.

Rigid foam slabstock and boardstock*Maddison and Vangronsveld (2000)*

Amine catalysts, fire retardants, glycols, blowing agents and flushing agents.

Acton (2001)

VOCs and toluene.

MDI and TDI: summary of release and abatement data

In Table 2.27 are summarized the data detailed in previous tables.

Table 2.27 Summary of pre-abatement releases.

| Application | Concentration | Annual loss | Release | Release based on estimated annual usage of diisocyanate |
|--------------------------------------|---------------------------------|-------------------------------|--------------------------------|---|
| | mg/m ³ | g | g/tonne | % |
| MDI | | | | |
| Rigid foam block | 2 to 4 × 10 ⁻³ | 20 to 25 | (3 to 7) × 10 ⁻³ | (6 to 10) × 10 ⁻⁷ |
| Boardstock (flexible facings) | <0.4 to 1.5) × 10 ⁻³ | <1 to 76 | (<8 to 250) × 10 ⁻⁴ | — |
| Boardstock (rigid facings) | <0.01 to 0.05 | <10 to 300 | (<2 to 350) × 10 ⁻³ | (<3.0 to 500) × 10 ⁻⁷ |
| Fibreboard | 0.05 to 1.3 | — | — | — |
| Oriented strand board | 0.2 to 0.4 | — | — | — |
| Flexible foam moulding | (0.1 to 10) × 10 ⁻³ | <2 to 26 | (2 to 200) × 10 ⁻² | (2 to 60) × 10 ⁻⁵ |
| Flame lamination | 48 × 10 ⁻³ | — | — | — |
| Prepolymer manufacture | <10 × 10 ⁻³ | — | — | — |
| Shoe-sole manufacture | <10 × 10 ⁻³ | — | — | — |
| Elastomers | 3 × 10 ⁻³ | — | — | — |
| TDI | | | | |
| Flexible foam slabstock ^a | 0.2 to 8 | — | 25 to 50 | (2.5 to 5.0) × 10 ⁻³ |
| Flexible foam moulding | 0.004 to 0.5 | (1.8 to 14) × 10 ³ | 1 to 28 | (0.6 to 9) × 10 ⁻³ |
| Flame lamination | 0.05 to 2 | — | — | — |
| Hot-wire cutting | 4 to 6 | — | — | — |
| Elastomers | 3 × 10 ⁻³ | — | — | — |

Conversion factors: for vapour,

MDI 1 mg/m³ ≡ 0.096 ppm;TDI 1 mg/m³ ≡ 0.14 ppm.

Saturated vapour concentrations (50 °C):

polymeric MDI 1 to 2 × 10⁻² µg/m³;TDI 1.2 × 10⁶ µg/m³.^aResults of Tu and Fetsch (1980), Chapman (2001) and Maddison and Vangronsveld (2000) (Table 2.18), combined.

In Table 2.28 are given data collected on the abatement of TDI emissions. There are no MDI abatement data available because the unabated releases were lower or much lower than the prevailing regulatory limits.

The values given in Table 2.27 are drawn from the studies cited in previous sections of the text. The ranges of results are probably representative of the global scene, given that the studies were of the applications consuming most of the MDI and TDI used worldwide, and given that the same proprietary manufacturing processes for these applications are found worldwide.

The key parameter is *mass loss of diisocyanate per mass of diisocyanate processed*, based on a per annum calculation, whether as g/tonne or % diisocyanate lost. Ex stack concentration is a less fundamental parameter, being inversely proportional to the volume flow of exhaust ventilation air, to an approximation. Releases of MDI range from <6 × 10⁻⁷ % to 6 × 10⁻⁴ % of total MDI

Table 2.28 Summary of TDI abatement data.

| Application | Pre-abatement concentration mg/m ³ | Post-abatement concentration mg/m ³ | Abatement % | Notes |
|--------------------------------|--|---|----------------|-----------------|
| Flexible foam slabstock | | | | From Table 2.25 |
| Polyether foam | 0.8 to 3.0 | <0.001 | ca 100 | |
| Polyester foam | 0.25 | 0.006 | 98 | |
| Flame lamination | | | | From Table 2.26 |
| Polyether foam | 0.25 to 2.1 | <0.02 | 90 to 99 | |
| Polyester foam | 0.42 | <0.02 | >94 to >96 | |

throughput, which equate to a range of <0.8 mg/tonne to 2 g/tonne, in the very high volume rigid boardstock and rigid foam slabstock sectors. Losses of TDI range from $2.5 \times 10^{-3} \%$ to $9 \times 10^{-3} \%$, which equate to the range of 1 to 90 g/tonne TDI, for the dominant TDI usage sectors of flexible foam slabstock and moulding.

The unabated concentration and annual loss values for MDI were extremely low, and below all ex stack limits which applied, the most stringent of which was (and still is in 2002) 0.1 mg NCO group/m³ (equivalent to 0.3 mg MDI/m³) as required by the UK Environment Agency. Accordingly, the values calculated for the efficiency of abatement (Table 2.28) relate to TDI or TDI-based polyurethane (flame lamination) only.

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