HEALTH AND SAFETY IN EMPLOYMENT ACT 1992

Approved Code of Practice for the

SAFE USE OF ISOCYANATES

OCCUPATIONAL SAFETY & HEALTH SERVICE

DEPARTMENT OF LABOUR
TE TARI MAHI

Published by the Occupational Safety and Health Service
Department of Labour
Wellington
New Zealand

March 1994

ISBN 0-477-03454-3

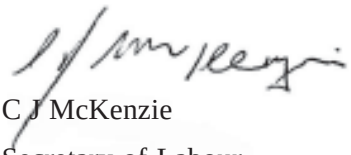
$10 (incl. GST)

P501/080/4000/1994

CONTENTS

NOTICE OF ISSUE

I have issued this *Approved Code of Practice for the Safe Use of Isocyanates*, being a statement of preferred work practices or arrangements, for the purpose of ensuring the health and safety of persons to which this code applies and persons who may be affected by the activities covered by the code.



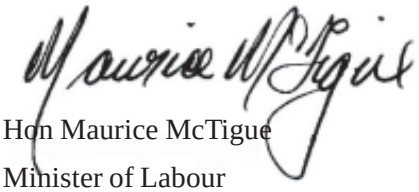
C J McKenzie

Secretary of Labour

June 1993

FOREWORD

I have approved this statement of preferred work practices, which is an *Approved Code of Practice for Safe Use of Isocyanates* under Section 20 of the Health and Safety in Employment Act 1992. When a code is approved, a Court may have regard to it in relation to compliance with the relevant sections of the Health and Safety in Employment Act. This means that if an employer in an industry or using a process to which an approved code applies can show compliance with that code in all matters it covers, a Court may consider this to be compliance with the provisions of the Act to which the code relates.



Hon Maurice McTigue

Minister of Labour

June 1993

SUMMARY OF THE HEALTH AND SAFETY IN EMPLOYMENT ACT 1992

The principal object of the Health and Safety in Employment Act 1992 is to prevent harm to employees at work. To do this it imposes duties on, and promotes excellent health and safety management by, employers. It also provides for regulations and codes of practice that set more detailed minimum standards.

The following information is a brief outline of provisions of the HSE Act. Copies of the Act and associated regulations may be purchased from any GP Books shop or any Occupational Safety and Health Service branch offices.

APPROVED CODES OF PRACTICE

The Act allows for the development and approval of statement of preferred work practice, known as "approved codes of practice". These are recommended means of compliance with provisions of the Act, and may include procedures which could be taken into account when deciding on the practicable steps to be taken. Compliance with codes of practice will not be mandatory. However, they may be used as evidence of good practice in Court.

EMPLOYERS

Employers have the most duties to perform to ensure the safety and health of employees.

If you are an employer then you have a general duty to take all practicable steps to ensure the safety of employees while at work. (This is set out in section 6.) In particular, you are required to take all practicable steps to:

- Provide and maintain a safe working environment;
- Provide and maintain facilities for the safety and health of employees at work;
- Ensure that machinery and equipment in the place of work is designed, made, set up, and maintained to be safe for employees:
- Ensure that employees are not exposed to hazards in the course of their work; and
- Develop procedures for dealing with emergencies that may arise while employees are at work.

HAZARD MANAGEMENT

Employers must identify hazards in the place of work (previously existing, new and potential) and regularly review these to see whether these hazards are significant and require further action. Where an accident, serious harm or an event, which in different circumstances might have caused harm to any person occurs, an employer must record it in a register of a prescribed form. The employer must also investigate whether it was caused by a significant hazard.

"Significant hazard" means a hazard that is an actual or potential cause or source of—

(a) Serious harm; or

(b) Harm (being more than trivial) the severity of whose effects on any person depend (entirely or among other things) on the extent or frequency of the person's exposure to the hazard; or

(c) Harm that does not usually occur, or usually is not easily detectable, until a significant time after exposure to the hazard.

Where the hazard is significant, the Act sets out the steps an employer must take.

- Where practicable, the hazard must be eliminated;
- If elimination is not practicable, the hazard must be isolated;
- If it is impracticable to eliminate or isolate the hazard completely, then the employer must minimise the hazard to employees. In addition, the employer must, where appropriate:
  - Ensure that protective clothing and equipment is provided, accessible and used;
  - Monitor employees' exposure to the hazard;
  - Seek the consent of employees to monitor their health; and
  - With informed consent, monitor employees' health.

Employers must establish systems for this process of identifying and managing hazards. In situations where exposure to the hazard can only be minimised, the employer must ensure the systems put in place to protect the employee are used. Employers need to involve employees in the development of systems and emergency procedures to be used (section 14).

INFORMATION FOR EMPLOYEES

Before an employee begins work their employer must inform them of:

- Emergency procedures;
- Hazards the employee may be exposed to while at work;
- Hazards the employee may create while at work which could harm other people;
- How to minimise the likelihood of these hazards becoming a source of harm to others; and
- The location of safety equipment.

The employer is also required to inform employees of:

- The results of any health and safety monitoring. In doing so, the privacy of individual employees must be protected.

The employer must ensure employees are either sufficiently experienced to do their work safely or supervised by an experienced person. In addition, the employee must be adequately trained in the safe use of equipment in the place of work, including protective clothing and equipment (section 13).

An employer is also responsible for the health and safety of people who are not employees. An employer must take all practicable steps to ensure that an employee does not harm any other person while at work, including members of the public and other visitors (section 15).

EMPLOYEES

Effective safety management should involve everyone in a place of work. Employers have specific responsibilities but employees should look after themselves. If you are an employee, then the Act gives you responsibility for your own safety and health while at work. You must also ensure that your actions do not harm anyone else.

1. INTRODUCTION

The aim of this code of practice is to provide for the safety and protection of health of all personnel involved in industrial processes which use isocyanates. Its purpose is to give enough information so that a well-operated plant will follow from the observation of the code. The intention is to display the approach needed to all aspects of design and operation of the plant to make the use of isocyanates a safe procedure.

Isocyanates are chemicals used in the production of polyurethane materials. In New Zealand the manufacture of flexible and rigid polyurethane foam accounts for the bulk of isocyanate usage, with polyurethane paints and lacquers also having considerable importance. Further products using isocyanates are urethane rubbers, adhesives and binders.

Sections 2 to 6 are general provisions applicable to all isocyanate users. Sections 7 to 9, while aimed primarily at the foaming industry, should, with the necessary modification, be used by other industries using isocyanates such as paint manufacturers and the printing industry.

2. INTERPRETATION

2.1 ISOCYANATE CLASSIFICATION

Because of significant differences in volatility between the various common isocyanates, it is convenient to divide them into two classes based on these volatilities. TDI class isocyanates have significantly greater volatilities at a given temperature than do MDI class isocyanates. The division into classes and its implications for precautions relating to health and safety are discussed in section 6.6 of the code.

2.2 SCALE OF USAGE

Three different categories based on the scale of operation, i.e. low user, medium user and high user are defined in this code (see section 6.6.6).

3. DEFINITIONS

Act: Means the Health and Safety in Employment Act 1992.

Employer: In this code the term employer is taken to include principals, contractors, subcontractor, or person who controls a place of work as defined by the Act.

Inspector: Unless specified, means an inspector appointed under the Act.

MSDS: Material Safety Data Sheet.

OSH: Occupational Safety and Health Service of the Department of Labour.

Standard: Means the current standard published by Standards New Zealand or an equivalent overseas organisation. A list of the relevant standards current at the time of publication is appendixed, however, as they are regularly updated their current status should be checked.

Regulation: Unless specifically defined, means a regulation made pursuant to the Act or a regulation made pursuant to the Factories and Commercial Premises Act 1981, that has not been repealed by the Act.

WES: Workplace Exposure Standards are guidelines for assessing the adequacy of the measures taken to limit exposure to airborne substances in the workplace. The WES booklet is updated and published regularly by OSH. It is obtainable from OSH branch offices.

BEI: Biological Exposure Indices as described in the WES booklet.

TWA: Time Weighted Average as described in the WES booklet.

STEL: Short-Term Exposure Level as described in the WES booklet.

4. RELATED LEGISLATION

While this code specifically deals with isocyanates there is other legislation with more general application which also should be considered. A list of this legislation current at the date of publication is given in appendix 9.

5. CHEMICAL DATA

5.1 PROPERTIES

Organic isocyanates are chemicals characterised by the general chemical formula R(NCO)x. The two most commercially important isocyanates are toluene diisocyanate (TDI) which is also known by the synonyms tolylene diisocyanate or toluylene diisocyanate, and 4,41 diphenylmethane diisocyanate (MDI) which has the synonym methylene bis (4-phenylisocyanate). The abbreviations TDI and MDI are now universally used and understood in the industry.

The table on the following page summarises the principal properties of commercially available TDI and MDI in the form of pure products or mixtures of isomers and oligomers that constitute the bulk of the market. Properties of solvent-based systems and prepolymers are not given because of their wide variation in composition.

5.2 REACTIVITY

Both TDI and MDI are denser than water and will sink to the bottom of water-filled containers. Although they react with water, the rate of reaction is very slow at temperatures below 50°C. At higher temperatures the reaction of TDI and MDI with water liberates carbon dioxide gas and a solid, insoluble mass of polyureas is formed.

TDI and MDI will also react with basic materials such as sodium hydroxide (‘caustic soda’), ammonia, primary and secondary amines and with acids and alcohols. The reaction may be violent, generating heat which can result in an increased evolution of isocyanate vapour and formation of carbon dioxide leading to a build-up of pressure within closed containers.

The high reactivity of isocyanates is the basis for the poly-addition process for preparation of polyurethane plastics and foams.

Neither TDI nor MDI is generally corrosive towards metals (except aluminium) at ambient temperatures.

Principal Properties of Commercially Available TDI and MDI

	TDI	**MDI**
Physical state at normal temperatures	Liquid (thin)	Liquid (oily)
Colour	Colourless to pale yellow (clear)	Dark brown (opaque)
Odour	Pungent (characteristic)	Earthy, musty (characteristic)
Specific gravity (at 25°C)	1.22	1.23
Boiling Point (°C)	250	Polymerises about 260°C with evolution of carbon dioxide
Flash Point (°C)	127	Over 200
Fire Point (°C)	145	Over 200
Freezing Point (°C)	Below 14	Below 10*
Vapour Density (air = 1)	6.0	8.5
Vapour pressure (mbar at 25°)	3×10^{-2}	Below 10^{-4}
WES** (ppm) (mg/m^3)	0.02 0.14	0.02 0.2

*pure MDI = 38°C
** See Appendix 1

6. HAZARDS AND HAZARD CLASSIFICATION

6.1 GENERAL

6.1.1 All isocyanates are potentially hazardous materials and require care in handling. From the practical point of view the principal hazard arises from the vapour (rather than the liquid) and hence the degree of hazard depends on the vapour pressure of the particular isocyanate concerned.

6.1.2 In the case of TDI the vapour pressure is such that at normal temperatures the concentration of vapour in air will exceed the WES. Hence, full precautions are necessary whenever TDI or TDI-containing products are handled.

6.1.3 By contrast, MDI has a lower vapour pressure at atmospheric temperature and with adequate ventilation a vapour concentration approaching the WES is not reached. However, two exceptions are (a) spray applications where airborne droplets (aerosols) present a hazard at normal temperatures; and (b) the dust arising from the handling of pure MDI (solid at normal temperatures). Full precautions must be taken in both these instances.

6.1.4 It should be noted that detection of isocyanates by smell is dangerous as the odour threshold is above the WES although the actual odour threshold will vary from individual to individual.

6.2 BREATHING OF VAPOUR, AEROSOLS AND DUSTS

6.2.1 Vapours, aerosols and dusts of isocyanates will irritate the membranes of the nose, throat, lungs and eyes. Exposure will produce a variety of symptoms which may include watering of the eyes, dryness of the throat, tightness of the chest (and sometimes difficulty with breathing) and headaches. The onset of the symptoms may be delayed until several hours after exposure has taken place.

6.2.2 After prolonged exposure some individuals may become sensitised. The sensitivity reaction takes the form of an asthmatic attack which may occur immediately or some time after exposure. Individuals may also become sensitised after a single high exposure. Once sensitised, individuals may exhibit asthmatic symptoms when subsequently exposed to atmospheric concentrations well below the WES.

6.3 EFFECT ON EYES

6.3.1 Isocyanates in the form of vapour, aerosol, liquid or dust irritate the eyes causing watering and discomfort and can cause permanent damage. In particular, splashes from reacting foam represent a severe hazard to the eyes.

6.4 EFFECT ON SKIN

6.4.1 Isocyanates have a mild tanning action on the skin. Occasionally contact dermatitis is produced as a manifestation of a specific skin allergy.

6.5 HAZARDS FROM UNDESIRABLE REACTIONS

6.5.1 WATER

6.5.1.1 Isocyanates react slowly with water to produce carbon dioxide. While this is not in itself a hazardous reaction, it can lead to the development of dangerous pressures inside closed containers if the isocyanate becomes contaminated with water.

6.5.2 RUBBER AND PLASTICS

6.5.2.1 Isocyanates will attack and embrittle many plastic and rubber materials in a short time. Others such as butyl rubber have a reasonable life span. If materials like butyl rubber are used, they must not be located in a position where rupture would cause a large spillage and must be checked regularly and replaced where necessary. Hoses of PTFE (Fluon or Teflon) suitably metal braided on the outside must be used on high pressure machines.

6.5.3 HEATING POLYURETHANE

6.5.3.1 Thermal decomposition of polyurethane materials may lead to the evolution of free isocyanate and a number of toxic gases, in particular carbon monoxide and hydrogen cyanide. The temperature at which this occurs varies according to the type of polyurethane and the availability of oxygen. In general, polyurethane starts to decompose between 150° - 300°C. Hydrogen cyanide and carbon monoxide are evolved at approximately 500°C. Temperatures between 300° and 400°C have been found to cause the evolution of free isocyanate.

6.5.3.2 Tasks which may involve exposure to isocyanates due to the heating of polyurethanes include soldering wire coated with polyurethane plastic, “hot-wire” cutting of polyurethane foam, welding pipes lagged with polyurethane foam and burning off polyurethane paint.

Refer to section 5.2 for details of reactions with particular chemicals.

6.6 HAZARD CLASSIFICATION AND SCALE OF OPERATION

6.6.1 The actual hazard associated with the use of isocyanates depends not only on the toxicity of the isocyanates, but also on their volatility and the quantity used in a particular operation. TDI is over 200 times more volatile than MDI at room temperature and thus the hazard posed by similar quantities of these two materials is far greater for TDI. This means that safety provisions must be much more stringent for TDI. This is reflected in the requirements for TDI as compared to MDI in sections 7 and 8 of this code, where the hazards are considered under two classes, a TDI class and an MDI class.

6.6.2 Isocyanates with a high vapour pressure are considered to be in the TDI class. These include TDI and HDI.

6.6.3 Isocyanates with a low vapour pressure are considered to be in the MDI class. These include MDI itself, NDI, PAPI, IPDI, TMDI, and surface coating materials (e.g. paints, lacquers) based on MDI. Appendix 1 contains further details of the various isocyanates.

6.6.4 Prepolymers for foaming processes, and surface coating materials containing partially polymerised isocyanates (produced from TDI, HDI or mixtures of these with IPDI) are considered to be in the MDI class if they have levels of free TDI or HDI below 0.7%. However, if a surface coating is to be sprayed, then for the purposes of respiratory protection the prepolymer is considered to be in the TDI class (see sections 9.4.7 and 9.5).

6.6.5 When materials in the MDI class are heated above a temperature of 50°C they shall be considered as materials in the TDI class. This is a generality only and may not hold in a particular case.

6.6.6 The scale of operation will be divided into three groups based on the isocyanate usage rather than the amount of polyurethane material produced. When more than one operation exists in a factory, consideration would be given to classifying the operations separately.

6.6.7 When the scale of operation is below 0.001 tonne (1 kg) of isocyanate per day and below 0.1 tonne (100 kg) of isocyanate per year, then the occupier will be termed a low user of isocyanates.

6.6.8 When the scale of operation is greater than that of a low user and below 1 tonne of isocyanate per day and 100 tonnes of isocyanate per year, then the occupier will be termed a medium user of isocyanates.

6.6.9 When the scale of operation is above 1 tonne of isocyanate per day or above 100 tonnes of isocyanate per year then the occupier will be termed a high user of isocyanates.

7. PLANT DESIGN

7.1 GENERAL

7.1.1 All production plant shall be designed with the following criteria in mind:

(a) The system must not allow isocyanates to escape into the atmosphere, and

(b) As isocyanates will react with water under most conditions, every attempt must be made to eliminate water, as both liquid and vapour, from the system.

In all plant design and operation the current WES levels must not be exceeded. (See appendix 1.)

7.2 VENTILATION

7.2.1 GENERAL

7.2.1.1 Buildings or rooms in which isocyanate materials are stored, handled or processed must have sufficient ventilation provided to ensure that the relevant WES is not exceeded at any time. Natural ventilation will provide some of the ventilation required but often this will have to be supplemented by mechanical extraction.

7.2.1.2 Extraction points shall be located as close to the point of potential hazard as is practicable. In areas of low air movement, regard must be had for the high density of isocyanate vapour, with extraction points being located near ground level.

7.2.1.3 Intake points shall be sited as far as practicable from outlet ducts to avoid recycling of polluted air.

7.2.2 TDI

7.2.2.1 Wherever practicable, totally enclosed systems shall be employed whenever TDI class isocyanates, or other isocyanates heated above 50°C, are used. The addition and removal of these isocyanates from the systems should be carried out without the need to have any part of the process plant open to the atmosphere.

7.2.2.2 Whenever opening of the above plant is unavoidable, such as for maintenance, then sufficient additional ventilation shall be provided to keep vapour from isocyanates below the WES.

7.2.2.3 Ventilation units must be installed on or about the equipment when plant design is such that vapours from TDI class materials could otherwise escape into the atmosphere.

7.2.2.4 Where hoods are required for TDI class materials then the following design principles must be applied (see figures 1 and 2):

(a) The process must be enclosed as much as possible;

(b) The extraction hood must be located as close as possible to the source of the escaping vapour;

(c) The hood face velocities must be sufficient to ensure that the WES is not exceeded in the breathing zone of the operator. The actual rate of air movement required will depend upon the physical design of the booth and extraction equipment.

(d) The vapours should be drawn away from the operator's breathing zone;

(e) Baffles and side shields should be used to the fullest extent; and

(f) The hood should be positioned so that it does not interfere with the operator's work.

7.2.2.5 The ventilation system should be electrically or pressure interlocked so that it is impossible to start foaming (or other similar processes) with TDI class materials without the exhaust fans running. There should also be a timedelay switch on all continuous foam processes which is so arranged that the ventilation continues for at least half an hour after processing has ceased. Alternatively, permanent low-level ventilation should be supplied. This equipment is essential for high users of TDI (i.e. those whose usage rate is above 1 tonne per day or 100 tonnes per year) and is recommended for other users of non-trivial quantities.

7.2.3 MDI

7.2.3.1 Plant handling MDI class materials need special precautions only if there are operations in which the material is foamed into open moulds and the WES is thus likely to be exceeded, or where there is a dust hazard from powdered isocyanates. However, if the reaction temperature during production of MDI-based rigid foam exceeds 50°C, as is often the case, then enclosure of the process and effective ventilation of this enclosure will be essential.

7.2.3.2 For MDI class materials a hood with a face velocity of 0.5 m/sec should be located above these operations if this is practicable. Otherwise protective equipment must be worn.

EXAMPLES OF EXTRACTION HOODS FOR TDI CLASS MATERIALS

For TDI Materials

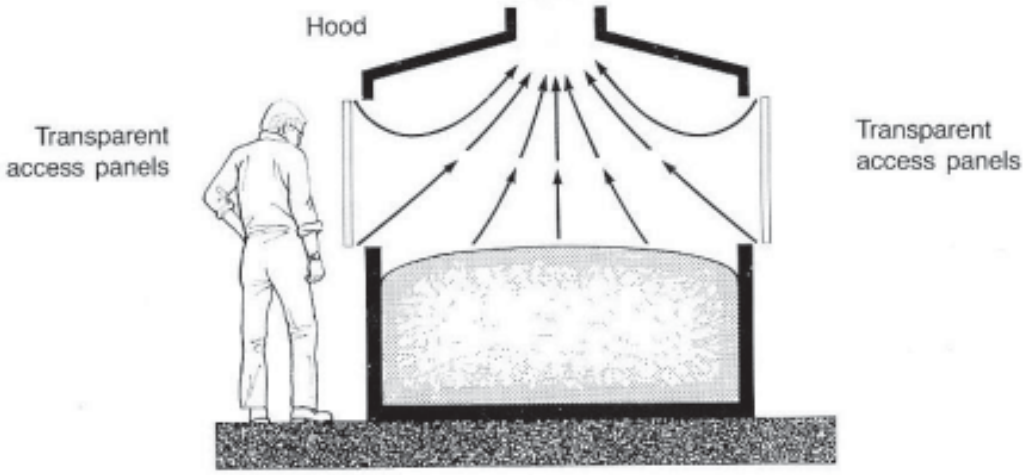


Fig. 1 Polyurethane foam block plant

For MDI Materials

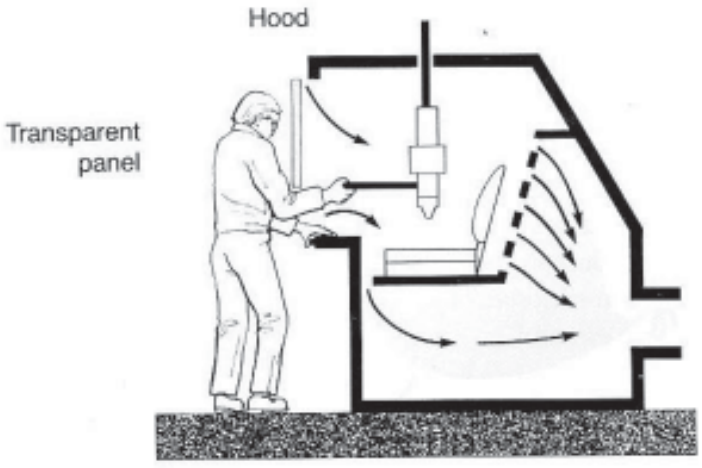


Fig. 2 Polyurethane foam mould filling

7.3 DRUM HANDLING AND STORAGE

7.3.1 GENERAL

7.3.1.1 Drums should be placed on their sides, restrained from movement by suitable chocks, and stored in an area with adequate ventilation.

7.3.1.2 The handling and storage area may be either inside or outside the factory. Outside storage is recommended only for situations where drums do not remain outside for long enough to corrode.

7.3.1.3 Drums damaged in transit and found to be leaking must be isolated and treated as a health hazard.

7.3.1.4 Any drum which has become pressurised must be isolated immediately and covered. The pressure must be subsequently relieved as soon as possible by carefully loosening the bung or drilling a small hole.

7.3.2 TDI

7.3.2.1 In order to thaw frozen drums of TDI they must be heated slowly using a well ventilated oven or hot chamber. The oven temperature shall be controlled below 35°C. For prolonged storage the suggested maximum is 30°C.

7.3.2.2 In no circumstances shall drums of TDI be thawed by using a naked flame or other forms of localised heating.

7.4 DRUM EMPTYING

7.4.1 GENERAL

7.4.1.1 Isocyanates must not be displaced from drums by pressurising because of the problem of ultimate venting of the empty drum and the risk of an explosion.

7.4.2 TDI

7.4.2.1 A gate valve, PTFE lined diaphragm valve or other valves in stainless steel or nylon should be fitted to the 50 mm diameter opening and an elbow of gas piping containing gauze and dry silica gel should be fitted to the 20 mm diameter opening. A drip tray containing solid decontaminant, e.g. impregnated sawdust, should always be provided and adequate supplies of liquid decontaminant should be available close to hand. (See appendix 3 for further information on decontamination mixtures.)

7.4.2.2 After the appropriate fittings have been made, small quantities of TDI class materials can be conveniently drawn off from a drum by placing it in a horizontal position.

7.4.2.3 To discharge appreciable quantities of TDI materials from a drum, it should be stood end uppermost and a stand pipe introduced and secured through the 50 mm diameter opening. A silica gel drier should be fitted over the 20 mm diameter opening so that when the contents of the drum are discharged by pumping, the displacement is filled with dry air. Wherever possible, direct discharge into the reactor kettle or machine through flexible hosing and suitable sealed connections is recommended so as to minimise the chance of spillage.

7.4.3 MDI

7.4.3.1 Similar methods should be used for emptying drums of MDI class materials except that the drip tray need not contain solid decontaminant. This method is not necessary for polyurethane paints and lacquers.

7.5 BULK STORAGE, TANKS AND LINES

7.5.1 GENERAL

7.5.1.1 All tanks in which TDI and MDI class materials (except polyurethane paints and lacquers) are stored should be blanketed with a dry gas, such as nitrogen, or with dry air or by locating a drying agent in the air vent. The air vent should be a conservation type which vents off to a safe area.

7.5.1.2 In general, plain steel equipment is satisfactory for storing isocyanates. A tank may be lined with a heat cured phenolic coating to prevent discolouration during storage. Linings will be unnecessary with careful control of moisture.

7.5.1.3 Stainless steel pipelines and tanks are perfectly satisfactory but their cost is not warranted unless it is essential that the absolute minimum of colour be maintained, as is the case in the production of clear coatings. However, the cleanability of bright finish type 316 stainless steel is excellent. This is therefore recommended for connections that are sometimes exposed to the atmosphere.

7.5.1.4 Flexible hoses should be reinforced and valves used for handling TDI and MDI class materials should either be PTFE and/or nylon-lined. Stainless steel valves are also suitable and so is butyl rubber hose, provided it is used no longer than six months as it hardens and will eventually crack.

7.5.2 TDI

7.5.2.1 Where TDI is heated by means of a heat exchanger, the temperature of the TDI shall be automatically controlled to no greater than 30°C.

7.5.2.2 To avoid the risk of over-filling, storage tanks for TDI class materials should have the following instrumentation:

(a) A fully enclosed level gauge (magnetic type or float using level tape preferred);

(b) A temperature indicator; and

(c) A high level alarm.

The use of a standard sight glass or manual dipping is prohibited.

7.5.2.3 Aluminium is not recommended for direct contact with TDI because of the possible corrosion and subsequent contamination of the TDI.

7.5.2.4 If ambient temperatures require it, lines, valves and tanks containing TDI should be lagged and heated by steam or electric tape trace to prevent freezing. After each use traced lines should be blown clear to prevent overheating and consequent discolouration provided the lines are self-draining. Otherwise it is better to leave the lines filled and turn off the trace heating. To avoid overheating, provision of suitable high temperature alarm systems should be made.

7.5.2.5 Process vessels which are emptied and/or filled with TDI class materials must have their air vents extended out through the roof of the factory or some other means must be used to prevent vapours escaping into the work area. The vents should be designed in such a way that moisture does not get back into the process vessels.

7.5.2.6 A suitable cartridge type filter is desirable in the isocyanate supply line from bulk storage to the process.

7.6 PUMPS AND FILTERS FOR TDI CLASS MATERIALS

7.6.1 Submersible glandless pumps shall be used to prevent leakage from glands. These pumps should also eliminate air entrainment which could adversely affect the process. A submersible pump should be immersed in a tank of suitably inert liquid (e.g. dioctyl phthalate) when it is not in use.

7.6.2 Filters for TDI class materials should be drainable before opening and capable of being cleaned from the top in order to prevent spillages. Down-draught ventilation adjacent to the filter is recommended.

7.7 MOULDS

7.7.1 It is important that foam moulds should be adequately braced to withstand the pressure arising from the foaming process when either TDI or MDI class materials are used.

7.8 STORAGE OF FOAMED MATERIAL

7.8.1 GENERAL

7.8.1.1 Newly-made hot foam slab stock must be stored in a separate well-ventilated area with fire resistant walls. It must not be moved to the other process areas until the exothermic reaction has ceased and a reasonable amount of internal cooling has taken place. The time for this cooling period

varies with the grade of foam. Therefore, newly-made foam blocks should not be stacked or brought into contact with one another until an appropriate degree of cooling is achieved.

7.8.1.2 Bulk stocks of polyurethane foam can burn quickly and rapidly, giving off various poisonous gases (e.g. carbon monoxide) and large amounts of hot dense smoke.

7.8.1.3 Self-contained breathing apparatus must be used in fighting this kind of fire. The temperature of the smoke and fumes from the polyurethane foam creates an additional hazard. This danger is present regardless of whether or not flame-retarded or flame-proofed foams are involved.

7.9 DUST FROM CURED FOAM

7.9.1 Dust generated during the machining of foam blanks, provided they are fully cured, should not present a problem apart from the general nuisance dust potential.

7.9.2 However, if it is still in the process of undergoing curing, foam must be treated as if it contains free isocyanate and the appropriate precautions must be taken to ensure that no workers are exposed to hazardous levels of isocyanate vapour.

8. PLANT OPERATION, TRAINING AND SAFETY

8.1 EMPLOYEE EDUCATION, TRAINING AND RESPONSIBILITY

8.1.1 Employee training is probably the most important safety measure a company can take. Although great efforts can be put into protective equipment, operations and processes with safety in mind, an improperly trained person can create an undue hazard; therefore, personnel involved with isocyanates must be given job training before being assigned to duties involving the handling of isocyanates. This should cover the following aspects:

(a) the correct handling and storage of isocyanates;

(b) the hazards and symptoms of over-exposure to isocyanates;

(c) the necessity of reporting early symptoms;

(d) the procedure to be adopted in the event of a spillage, suspected leakage from valves, or suspected excess of isocyanates in the atmosphere;

(e) first aid procedures (see section 9.2); and

(f) personal hygiene recommendations.

8.1.2 It is recommended that an advisory leaflet written in the operator's first language covering the above points be given to employees at the completion of their job training. Appendix 4 gives an example suitable for translation.

8.1.3 Because prompt action may be needed in an emergency, it is important that process operators understand English or that supervisors can readily communicate with operators in their first language.

8.1.4 Induction training for personnel not directly concerned in the production of polyurethane material should mention the existence of hazards connected with the use of isocyanates. Isocyanate areas should be out of bounds to unauthorised persons.

8.1.5 All authorised visitors to the polyurethane process area must be warned of the hazard of isocyanates to any person with an asthmatic condition.

8.1.6 Personnel must abide by the requirements of the code where applicable, e.g. by not smoking in no-smoking areas. They must also wear or use protective clothing and/or equipment supplied by employers under the code.

8.2 INFORMATION AND WARNING

8.2.1 Process areas where isocyanate exposure is likely to occur shall have warning posters placed in prominent positions.

8.2.2 Signs shall be posted indicating the location of air respirators and/or air breathing equipment.

8.3 SPILLAGES

8.3.1 When spillages of isocyanate materials occur, there is the immediate risk that the concentration of isocyanate vapour in the atmosphere adjacent to the spillage will increase beyond the WES. Plans for handling spills must therefore be drawn up which provide for the protection of those dealing with the spillage and for the control and protection of other people in the vicinity so as to ensure that they do not suffer undue exposure.

8.3.2 Small spillages of MDI class materials (less than 1 litre) and very small spillages of TDI class materials (less than 10 millilitres) can be wiped up immediately with cotton waste (or treated with other absorbent material in the case of MDI class materials) and the area treated with decontamination mixture or isopropyl alcohol. The contaminated cotton waste (or absorbent material) must be decontaminated as soon as possible. Gloves should be worn by personnel handling these materials.

8.3.3 Spills of TDI class materials which are more than a few millilitres and large spills of MDI class materials must be treated according to the general procedures outlined in appendix 2.

8.3.4 After spills in the category described under section 8.3.3, personnel must not be permitted to return to the work area until air tests with appropriate equipment show the atmosphere to be below the WES.

8.3.5 A disaster plan shall be drawn up for accidents involving a major spillage of TDI class materials. This must include provision for total plant evacuation and involvement of the necessary emergency services.

8.4 WASTE DISPOSAL

8.4.1 Unreacted isocyanate shall not be disposed of under any circumstances and must first be transformed into urea by reaction with water. Liquid isocyanate must never be washed into a drain.

8.4.2 Isocyanate drums for disposal must be decontaminated and thoroughly cleaned before re-use or destruction. Methods of decontamination include:

(a) The use of decontamination mixture;

(b) Filling with water and leaving for 48 hours; and

(c) The use of waste polyol.

Drums must be vented during or after these procedures.

8.4.3 Returnable empty drums to be refilled with isocyanate should be completely drained and all openings tightly closed with gaskets in place. Care should be taken that no moisture is present since this will react with traces of isocyanate causing the generation of carbon dioxide, and the result could be the rupture of the drum.

8.4.4 Disposal of waste materials after treatment should be in accordance with local authority requirements.

8.5 EYE-WASH FACILITIES

8.5.1 Hygienic eye-wash facilities must be provided near the work area. These can take the form of a small rose fitting connected by tubing to a tap, a device which squirts water spray into the eyes when operated by the pressure of the forehead on a bar, or other suitable device. It is recommended that high users provide safety showers and eye wash facilities; that medium users provide eye wash facilities; and that low users supply eye-wash bottles (see sections 6.6.7 to 6.6.9).

8.6 RESPIRATORY PROTECTION

8.6.1 Administrative and engineering controls shall be used wherever feasible to maintain isocyanate vapour concentrations below the prescribed WES level. Respirators that comply with the current standards shall be provided and used for non-routine operations, where occasional brief excursions above the WES occur, and for emergencies.

8.6.2 The principles governing the choice of respirators shall be as follows:

(a) TDI Class Materials

(i) Compressed airline or self contained breathing apparatus respirators are to be used in areas where the WES level is likely to be exceeded such as the hot box for TDI drums, and in the follow-up to any plant emergency including spills or leaks greater than 10 millilitres, or in cases where the extent of the spill or leak is in doubt.

(ii) Full facepiece type (negative pressure) gas respirators fitted with the appropriate filter to remove organic vapours are acceptable for cleaning up known small spillages (less than 10 millilitres) provided workers' safety is not compromised. Half facepiece gas respirators with filters to remove organic vapours will be acceptable for the evacuation of other personnel during plant emergencies.

NOTE: When not in use, gas respirators must be stored in sealed airtight containers or plastic bags to prevent the filters from deteriorating due to exposure to traces of fumes present in the atmosphere.

(b) MDI Class Materials

Full facepiece or half facepiece (negative pressure) gas respirators are acceptable in all situations except when spraying reacting foam or paint. In these cases full facepiece airline or self-contained breathing apparatus respirators are to be used.

8.6.3 Respirators shall be placed in marked locations close to, but not in, process areas and shall be routinely tested and adequately maintained. Records of the exposure time of canister respirators must be kept and the canister changed at the required intervals.

8.7 PROTECTIVE EQUIPMENT AND CLOTHING

8.7.4 Protective equipment can he divided into 2 classes; normal protective equipment and emergency protective equipment. These terms are defined as follows:

(a) *Normal Protective Equipment* must be used with either MDI or TDI class isocyanates during all working operations where there is adequate ventilation and hence no possibility of exposure to amounts of vapour in excess of the WES (see appendix 1). This should include the following protective equipment:

Boiler Suit/Overall (heavy cotton types are preferred)

Rubber or PVC Gloves where there is a risk of skin contamination; and

Goggles or Face Shield where there may be a risk of eye hazards.

(b) *Emergency Protective Equipment* must be used with both TDI and MDI and isocyanate containing products wherever there is a risk of exposure to concentrations of vapour (or dust) in excess of the WES. Such conditions occur when:

(i) TDI is handled outside a properly ventilated area;

(ii) MDI is handled, heated, sprayed or involved in mixinghead cleaning operations outside a properly ventilated area; or

(iii) Pure MDI is handled in solid form and there is a risk of dust being created or raised.

Typical items of emergency protective equipment include:

Waterproofs suit

Rubber or PVC gloves

Rubber or PVC apron

Rubber boots and

Full-face breathing apparatus

8.8 CLEANING AND REPAIR OF TANKS AND ASSOCIATED EQUIPMENT USED FOR THE MIXING AND STORAGE OF ISOCYANATES

8.8.1 **Authorisation:** The cleaning of lines and tanks used for isocyanates will expose personnel to a greater hazard risk than normal operations. These

procedures must be carried out on the authorisation of a work permit issued by the factory manager or his nominee only. The person responsible must also be satisfied that the work is carried out under the direction of appropriately trained personnel who are familiar with the necessary procedures and safeguards.

8.8.2 **Work Permit:** A written work permit which covers the following elements shall be prepared:

(a) Work shall not he carried out by an unaccompanied person;

(b) Isolation procedure must eliminate electrical and mechanical hazards;

(c) Decontamination procedures must remove residual isocyanates left in the system;

(d) Atmospheres in confined spaces must be tested to ensure the air is safe to breathe;

(e) Unless airborne concentrations of isocyanates can be maintained below the appropriate WES, respiratory protection must be used;

(f) Adequate access and egress to and from confined areas must be provided; and

(g) Adequate rescue procedures must be established and suitable rescue equipment must be provided.

See appendix 5 for an example of a work permit.

8.8.3 On completion of the work the authorising officer shall sign the permit confirming that the plant is safe for use in process operations.

9. MEDICAL REQUIREMENTS

9.1 EMPLOYEE MEDICAL SURVEILLANCE

9.1.1 One of the early symptoms of isocyanate-induced respiratory illness is a dry cough, characteristically worse in the evening or at night, often obscuring the fact that it is due to the work environment. It is therefore necessary to take the following steps to protect the health of isocyanate workers.

9.1.2 Isocyanate users should arrange for a pre-placement health examination to be carried out on all employees who will be working with TDI class materials, or MDI class materials which are sprayed. This examination should be used to provide baseline medical data and to detect possibly susceptible individuals who should be advised against working with isocyanates. This health examination should include a review of the employee's medical history and, wherever possible, lung function tests. The health history review and lung function tests should be repeated within three months of beginning work with isocyanates.

9.1.3 Following the initial examinations, medical history reviews and lung function tests should be performed at least annually on all employees working with TDI class materials and MDI class materials which are sprayed.

9.1.4 All isocyanate users should arrange for a health examination, as described in section 9.1.3 to be carried out on any employee who experiences a cough lasting longer than four weeks, or a chest illness requiring an absence of two weeks or more from work.

9.1.5 If an unexplained fall in lung function is found, the work environment of the affected employee should be investigated and any employee showing respiratory distress, should not return to work with isocyanates. The lung function measurement should be repeated the next day and, if the diagnosis is confirmed, the employee should not return to work with isocyanates until cleared by a further medical examination.

9.1.6 The medical diagnosis of true sensitisation to isocyanates at any time must permanently exclude that person from further exposure to isocyanate materials.

NOTE: This does not preclude such people from being employed elsewhere in the factory where isocyanate exposure can be avoided.

9.1.7 After accidental over-exposure, such as after a spillage of either TDI or MDI class materials, all employees involved should have an examination (as described in section 9.1.3) two to four weeks after the incident so as to detect any harmful effects.

9.1.8 Smoking shall not be permitted where isocyanates are stored or used.

9.1.9 Records of the medical examinations and health surveillance checks mentioned in sections 9.1.2-4 and 9.1.7 should be kept by the firm and made available to the departmental medical practitioner or nominee. These records should be held for a period of at least 7 years after the employee has terminated employment with the firm.

9.2 FIRST AID

9.2.1 When it is known or suspected that workers have been exposed to isocyanate vapour levels above the WES, they should be removed from the contaminated area. Provided only limited exposure has occurred, only those steps described in section 9.1.7 need be carried out. However, it should be remembered that symptoms may not develop until many hours after such exposure.

If the exposure was severe and the worker has stopped breathing, the worker should be moved to an uncontaminated atmosphere and artificial respiration started immediately. The patient should be kept warm and should receive medical attention without delay.

9.2.2 In high-user establishments oxygen should always be available for use in emergencies by experienced personnel.

9.2.3 Splashes of isocyanate in the eye are irritant and may cause severe chemical conjunctivitis. If any chemical used in the foaming process enters the eyes, they should be irrigated with copious amounts of clean water for at least 15 minutes as soon as possible. It has been found that this will require the help of another person to hold the victim's eye open. Reacting foam is particularly dangerous if it enters the eye.

9.2.4 Contact lenses should be worn only if the eyes are covered with goggles or a face shield when working with isocyanates. Chemicals can get behind contact lenses and irreparable damage may occur to the eye while the lens is being removed prior to the irrigation required in section 9.2.3.

9.2.5 If appreciable amounts are swallowed, the affected person should be given between 250 and 500m1 of milk or water. Do not induce vomiting. Obtain medical attention as soon as possible. Small splashes accidentally swallowed should present no hazard. DO NOT give anything by mouth to an unconscious person.

9.2.6 It is important that any isocyanate spilled on the skin should be removed immediately by washing with soap and water, as isocyanates can cause dermatitis, and may cause sensitisation leading to dermatitis in a small number of individuals.

NOTE: If skin contact is extensive, the employee should immediately use the emergency shower if available or adopt some other method of achieving a thorough cleansing of the affected area (see section 8.5). With TDI class materials this is important because of the inhalation hazard. Solvents may cause dermatitis and should not be used.

9.2.7 Spillage onto the employee's clothing is also serious with TDI class materials, particularly because of the inhalation hazard. The affected person should enter the shower immediately and remove the contaminated clothes while under the shower. Changes of clothing should be provided for such an emergency.

9.3 ATMOSPHERIC TESTING FOR ISOCYANATES

9.3.1 It is necessary for high and medium users of TDI class materials and MDI class materials which are sprayed to take regular atmospheric measurements and to check that the ventilation system in the production area is working adequately.

9.3.2 The testing points for atmospheric measurements should be determined as a result of use experience. For example, in a plant producing flexible foam continuously the most likely points would be:

(a) foaming head platform - particularly in the breathing zone of the foaming head operator;

(b) side paper strip off;

(c) base paper strip off; and

(d) at the cutting point of the blocks.

9.3.3 The tests should also be carried out when the concentration is likely to be at its highest level. For example, in plant producing flexible foam continuously, the isocyanate concentration increases throughout the foaming operation and the highest concentration is found just after foaming has stopped (see section 7.2.2.5).

9.3.4 All high users of TDI class materials should operate a continuous TDI analyser (see Sections 9.3.6-9). The output recorded by the analyser should be held in such a place that it is available to employees and to representatives of OSH.

9.3.5 Medium users of TDI class materials should carry out tests at least once a week during operations and low users at least twice a year (for recommended methods see sections 9.3.6 to 9.3.9). If ambient air concentrations of isocyanates reach half the WES in either case, more frequent tests should be carried out. The results of all tests should be held in such a place as to be available to employees and to representatives of OSH.

9.3.6 Detector tubes can be used to measure aromatic isocyanates (but not MDI) and are recommended for use by low users or for checking that the WES is not exceeded in an area after spillage has been decontaminated.

9.3.7 Colorimetric methods are available for testing aromatic TDI class materials (including MDI). These are:

(a) the ICI method utilising paper colour comparison; and

(b) the Marcali method utilising liquid absorption.

These methods are recommended for use by medium users. Special methods are required when testing for aliphatic isocyanates.

9.3.8 Continuous analysers, which are capable of detecting both aromatic and aliphatic (e.g. HDI) isocyanates, should be used by high users.

9.3.9 Monitors for checking on personal exposure levels may be useful for investigating the individual work habits of those demonstrating possible symptoms.

9.3.10 With all users, if the WES is exceeded, an investigation must be carried out in order to find and correct the cause. Sampling must be repeated each time the isocyanate is used until the atmospheric release has been controlled.

9.3.11 No employee shall be allowed to remain in an area contaminated with isocyanate above the WES, unless wearing suitable respiratory protective equipment. In the event of an evacuation as the result of such an excess, further readings must be taken before personnel are allowed to return to the plant.

9.3.12 A register of results for all tests (including both positive and negative Detector tests) should be maintained. The action taken as the result of the WES being exceeded should be noted along with the names of the personnel exposed. This register should be retained for at least 12 months and should be made available to employees and representatives of OSH.

9.3.13 There shall be no requirement on the occupiers of spray painting premises to carry out any of the monitoring tests provided for in sections 9.3.1-12. This is because it is recognised that the WES will normally be exceeded in all spraying operations and therefore special precautions are required to protect workers (see section 10.4). Isocyanate monitoring, however, may be carried out periodically by OSH in a wide range of spray booths to maintain a check on the general degree of hazard present in the workplace.

9.4 CONTAMINATED DISCHARGES

9.4.1 Legislation relating to the discharge of contaminates into the atmosphere or onto land or water is administered by regional authorities and generally prohibits such activity (refer appendix 9).

9.4.2 Isocyanates readily form ureas in the presence of water and therefore water scrubbers attached to the exhaust ventilation system offer a useful control method. Water scrubbers are recommended for high users of TDI class materials. Alkali solutions are more effective than water and hence will increase scrubber efficiencies. Care must be taken to ensure that the use of water scrubbers to control emissions to the air does not give rise to the discharge of contaminants into waste water.

9.4.3 If firms are in any doubt concerning emissions or control equipment, the regional council shall be consulted.

9.5 LABELLING

9.5.1 All containers of isocyanates or products containing isocyanates should be clearly labelled (refer appendix 9).

10. APPLICATION OF POLYURETHANE PAINTS AND LACQUERS

10.1 GENERAL

10.1.1 Polyurethane paints and lacquers fall into the following categories:

(a) urethane oils and urethane alkyds (e.g. polyurethane varnishes);

(b) blocked isocyanates (e.g. some soldering fluxes); and

(c) polyisocyanates (e.g. one-pack moisture-cured and two-pack isocyanate-containing paints).

10.2 URETHANE OILS AND ALKYDS

10.2.1 In the case of the manufacture of urethane oils and alkyds, the standard precautions set down elsewhere in this code for the handling of free isocyanates must be observed. However, the final product contains no residue of free unreacted isocyanate and thus in the handling and use of these products no special precautions are necessary.

10.3 BLOCKED ISOCYANATE COATINGS

10.3.1 Blocked isocyanate coatings also contain no residue of free unreacted isocyanate, and thus the application of these materials poses no problems from that viewpoint. However, phenolic solvents may be present in the formulated paint and additional phenolic material may be released during heat curing processes. In these circumstances appropriate precautions for phenols must be taken. These must include protection (adequate ventilation and/or respiratory protection against inhalation of phenoliccontaining vapours and suitable protective clothing to prevent skin contact.

10.4 POLYISOCYANATES: APPLICATION BY SPRAY, BRUSH OR ROLLER

10.4.1 The great majority of industrially-used polyurethane coatings contain polyisocyanates and thus fall into category 10.1 (c) above. The remainder of this section is concerned with precautions to be observed in the handling and application of these materials.

10.4.2 MDI type paints are those paints based on polyisocyanates which contain less than 0.7% free TDI or HDI. These products are predominantly used in spray painting applications,

10.4.3 TDI type paints are all those paints containing more than 0.7% free TDI or HDI. They are usually designed for special-purpose applications.

10.4.4 **Mixing of Paints.** Both MDI and TDI class paints shall be mixed in wellventilated areas. The appropriate respiratory protection should be worn, as stated in section 10.4.6.

10.4.5 Where a spillage of an MDI class paint or lacquer occurs, the spillage shall be cleaned up immediately by spreading sawdust, sand or similar material over the spillage and placing the collected mixture in an outside bin. The area affected by the spill should be decontaminated with a solution of dilute ammonia and detergent or other decontaminating mixture (see appendix 3). Spillages of TDI class paints shall be treated as detailed in appendix 2.

10.4.6 APPLICATION BY BRUSH OR ROLLER

10.4.6.1 Where MDI class materials are applied by brush or roller, there is unlikely to he a problem from exposure to free isocyanates unless ventilation in the area is inadequate. In this latter situation, protection can be obtained by use of an on-nasal respirator fitted with the appropriate canister(s).

10.4.6.2 Where TDI class materials are applied by brush or rollers the area shall be well ventilated and on-nasal canister respirators worn. However, if there is doubt about the effectiveness of the ventilation then positive pressure airsupplied respirators must be used.

10.4.7 APPLICATION BY SPRAYING

10.4.7.1 The atomised liquid paint which emerges from a spray gun is in the form of a fine mist and is technically referred to as an aerosol. These aerosols are of a sufficiently small particle size that they can be inhaled, and also the increase in the surface area of the paint following atomisation results in an increase in the isocyanate vapour being evolved. In addition, spraying applications present a major hazard from isocyanate-containing paints when the aerosol which bounces back off the sprayed article enters the breathing zone of the operator. Therefore, the spraying of isocyanatecontaining paint represents a considerably increased hazard over the application of these materials by brush or roller.

10.4.7.2 A further factor to be considered is that the aerosols of some polyurethane paints may contain a substantial quantity of isocyanate prepolymer having unreacted isocyanate groups. The potential of these prepolymers to cause respiratory sensitisation and irritation is now considered, following recent research findings, to be no different from that of the free isocyanate monomer.

10.4.7.3 Because of the matters discussed in sections 10.4.7.1 and 10.4.7.2 it is clear that the difference in volatility (and therefore in hazard) between MDI class

and TDI class polyurethane paints ceases to be of importance when these materials are applied by spraying, and thus the two classes of paints must be treated identically in terms of the hazard posed when they are sprayed.

10.4.8 PRECAUTIONS TO BE ADOPTED FOR SPRAYING AND DRYING OF SPRAYED ARTICLES

10.4.8.1 Unless otherwise provided for in this code, all spraying and the drying of sprayed articles shall be carried out in accordance with the requirements of the Regulations.

10.4.8.2 The spraying of all isocyanate-containing paints must be carried out in a properly designed and constructed spray booth in which the air movement is provided by mechanical ventilation in accordance with section 10.4.8.3. The only exceptions to this requirement shall be those outlined in section 5. Tunnel booths or canopy booths provided with an up-draught air movement shall not be used for the application of paints containing isocyanates.

10.4.8.3 All spray booths shall be designed and installed so that they are capable of producing and maintaining within an empty room booth or at the working opening of a cabinet booth the air movement stipulated below:

(a) All booths including semi down-draught booths shall provide a uniform air movement of not less than 0.5 m/sec within the breathing zone of the operator. or

(b) In the case of a full down-draught booth, the minimum average downward air movement shall be not less than 0.20 m/sec and, in addition, no single grid position within the booth shall have a downward air velocity of less than 0.10 m/sec (see appendix 5 for method adopted by OSH for determining air movements).

NOTE: If more than one spray gun is installed or used in any spray booth, the air movement to be provided may need to be increased. Advice must be obtained from the nearest office of OSH.

10.4.8.4 The mechanical ventilation (fan belt driven) system provided must be interlocked with the air supply to the spray gun in such a manner as to ensure that the gun cannot be operated unless the mechanical ventilation system is in operation and producing and maintaining the air movement required by section 10.4.8.3. In the case of ventilation, fans driven directly off the motor shaft or via a gearbox an electrical interlock between the spray gun and the fan motor will suffice.

10.4.8.5 When operators whether spraying or not, are required to work inside a spray booth whilst spraying is in progress they shall wear one of the following types of airline respirator, a full facepiece type, or a half facepiece type with separate goggles, or a hood or helmet type to protect them from inhaling the isocyanate monomer and prepolymer in aerosol form.

10.4.8.6 The compressed air supply for the respirators must be taken from an uncontaminated source and be substantially free of carbon monoxide and

carbon dioxide. The supplied air shall be free from all odour and filtered to remove water, dust and oil mist. It is recommended that an alarm system should be fitted to the air-supply unit to warn the user whenever the pressure falls to the minimum safe level. (See appendix 6 for requirements for all compressed air systems.)

10.4.8.7 In addition to the recommended respiratory and eye protection (see section 10.4.8.5), spray operators shall wear overalls, gloves and a head covering in the case of respirators which leave the hair exposed.

10.4.8.8 Mechanical ventilation of the booth must be maintained after spraying ceases. until the work area is free of all residual spray mist. No person should enter the booth unprotected for at least 5 minutes after spraying ceases.

10.4.8.9 Positive-pressure spray room booths have the capability of providing a dust-free environment by ensuring no unfiltered air can enter the booth. To minimise the possibility of toxic vapours escaping, all entrances to these booths must be hermetically sealed. As an additional precaution, it is recommended that the over pressure within the booth be maintained at no more than 25 Pa. Neutral or negative-pressure booths are inherently safer and are preferred.

10.4.8.10 When small cabinet booths are used for operations such as the spraying of test samples and the inward air velocity has been increased to 1 m/sec or more, respiratory protection may not be necessary, provided no spray bounce back can occur. However, it is recommended that respiratory protection be provided and worn.

10.4.8.11 In all other cases where objects are being sprayed in cabinet booths and spray bounce back cannot be effectively controlled even at air velocities of 1 m/sec, or where the operator may need to partially enter the booth, he or she must wear an airline respirator. In these situations an air movement rate of 0.5 m/sec is acceptable.

10.5 SPRAYING OPERATIONS OUTSIDE OF SPRAY BOOTH

10.5.1 Where the regulations allow for objects to be sprayed outside of a spray booth then, the whole of the enclosed area shall be regarded as hazardous and respiratory precautions must be taken as detailed in sections 10.4.8.5-8. Warning signs shall be posted to prevent unauthorised personnel inadvertently entering the hazardous area.

10.5.2 Where spraying is carried out in the open air, all persons working within 15 metres of the spraying operation must be provided with and wear respiratory protection as detailed in sections 10.4.8.5-7. Warning signs shall be posted to prevent unauthorised personnel inadvertently entering the hazardous area.

10.6 CONSTRUCTION MATERIALS FOR SPRAY BOOTHS AND DRYING OVENS

10.6.1 The design, construction and construction materials used in any spray booth, combination spray and drying booth, and any drying oven used for the application and drying of articles coated with TDI or MDI class materials shall be in accordance with the requirements of the Regulation , or as alternatively specified in appendix 8.

10.7 ISOCYANATE OVER-EXPOSURE

10.7.1 SYMPTOMS

10.7.1.1 Vapours and spray mists containing free isocyanates are highly irritating to the eyes and respiratory tract, and may cause inhalation sensitisation. In sensitised persons even minute isocyanate concentrations may lead to severe asthmatic attacks. Respiratory effects may be delayed for several hours. The liquid may be irritating to the skin and cases of skin sensitisation have been reported,

10.7.1.2 Atmospheric over-exposure may lead to the following symptoms:

(a) sore eyes (conjunctivitis),

(b) running nose (rhinitis),

(c) sore throat (pharyngitis),

(d) coughing (bronchitis),

(e) wheezing, tight chest (asthma),

(f) fever, breathlessness and cough (pneumonitis).

10.7.2FIRST AID TREATMENT

10.7.2.1 **Inhalation**

This may be either from the vapour or from an aerosol. Remove the affected person to fresh air. Keep at rest. Obtain immediate medical attention.

10.7.2.2 **Eye Contact**

If isocyanate has entered the eyes, flush them immediately with direct mains water or sterile water from an eye wash bottle for at least 15 minutes, holding the eyelids apart. Obtain immediate medical attention.

10.7.2.3 **Skin Contact**

Wash the skin immediately with copious amounts of water and soap (if available). Remove heavily contaminated clothing immediately. Obtain medical attention if skin dermatitis appears. (Clothing should be decontaminated in an aqueous solution containing 2%-5% ammonia (SG 0.880) and 0.2%-0.5% liquid detergent for one hour and then laundered before re-use.)

10.7.2.4 **Ingestion**

DO NOT induce vomiting. If the person is conscious, give between 250 ml and 500 m1 of milk or water to drink. Take to hospital without delay.
DO NOT give anything by mouth to an unconscious person.

10.8 EMPLOYEE TRAINING

The training of painters using isocyanate-containing paints is an important safety measure which must be undertaken by every employer. The instruction and training must include the following aspects:

(a) The hazards and symptoms of over-exposure to isocyanates (see section 10.7.1).

(b) The necessity for wearing an airline respirator and other protective clothing during all spraying operations (see sections 10.4.7.1-3, 10.4.8.5. and 10.4.8.7).

(c) The procedures to be adopted in the event of a spillage (see section 10.4.5).

(d) First aid procedures (see section 10.7.2).

(e) The correct use and maintenance of respirators including their storage.

(f) Safe work procedures, methods and practices.

(g) The reporting of defects in safety devices and equipment.

10.9 REMOVAL OF POLYURETHANE PAINT

10.9.1 SANDING DOWN

10.9.1.1 When isocyanate paints are fully cured, i.e. have been applied for more than 24 hours at room temperature or heated for one hour at 70 °C, and are sanded down, the dust produced will not present an isocyanate hazard. This is because fully cured paints contain no free isocyanates. In such instances a dust mask should be worn to provide protection from the general nuisance dust present. Where new paint that may not be fully cured is sanded down, the dust will contain free isocyanates. A particulate respirator fitted with Class H filters, or an airline respirator should be worn. Where practical the use of wet sanding methods is recommended as a means of reducing the amount of dust generated.

10.9.2 WELDING/CUTTING OF PAINTED METAL

10.9.2.1 In panel beating operations where metal previously painted with isocyanate-containing paints is subject to an oxyacetylene or gas torch, the polyurethane paint will decompose and produce a number of toxic gases including carbon monoxide. Free isocyanates should not be formed or if they are only in such minuscule amounts that no specific precautions will be required. In this

respect polyurethane paints differ significantly from polyurethane foams (see section 6.5.3). However, the metal cutting operation itself will normally produce hazardous fumes and must be performed in a well ventilated area. Where there is any doubt concerning the effectiveness of the ventilation, workers must wear respiratory protection such as an airline respirator.

10.10 EMPLOYEE MEDICAL SURVEILLANCE

10.10.1 One of the early symptoms of isocyanate-induced respiratory illness is a dry cough, characteristically worse in the evening or at night, often obscuring the fact that it is due to the work environment. It is therefore necessary to take the following steps:

(a) Occupiers involved in spraying surface coatings containing free isocyanates or polyisocyanates must ensure that new employees are advised to undergo a preplacement health examination. This examination should be used to provide baseline medical data and to detect possibly susceptible individuals, who should be advised against working with surface coatings which are sprayed and contain free isocyanates or polyisocyanates. This health examination should include a review of the employee's medical history and lung function tests. The health history review and lung function tests should be repeated within 3 months of beginning work.

(b) Following the initial examinations, medical history reviews and lung function tests should be performed at least annually on all employees.

(c) Occupiers should also arrange for a health examination, as described in paragraph (b) to be carried out on any employee who experiences a cough lasting longer than 4 weeks, or a chest illness requiring an absence of 2 weeks or more from work.

(d) If an unexplained fall in lung function is found, the work environment of the affected employee shall be investigated and any employee showing respiratory distress must not return to work with surface coatings containing free isocyanates or polyisocyanates. The lung function measurement should be repeated the next day and, if the diagnosis is confirmed, the employee shall not return to work until cleared by a further medical examination.

(e) The medical diagnosis of true sensitisation to isocyanates at any time must permanently exclude that person from further exposure to isocyanate materials.

NOTE: This does not preclude such people from being employed elsewhere in the premises where isocyanate exposure can be avoided.

(f) Records of the medical examinations and health surveillance checks mentioned in paragraphs (a) (b) and (c) should be kept by the firm and made available to the departmental medical practitioner or nominee. These records should be held for a period of at least 7 years after the employee has terminated his/her employment with the firm.

10.11 ISOCYANATE MONITORING

10.11.1 It is acknowledged that the free isocyanate concentration present in the aerosol mist during spray painting in a correctly set up and operated booth will usually exceed the Workplace Exposure Standard. For this reason, worker protection must be guaranteed by wearing a full facepiece airline respirator or its equivalent (see section 10.4.8.5) and routine isocyanate monitoring is unnecessary. Isocyanate monitoring, however, may be carried out periodically by OSH the in a wide range of spray booths to maintain a check on the general degree of hazard present in the workplace.

10.12 LABELLING

10.12.1 A specific warning statement is required on all two-pack polyurethane and moisture-cured products to be applied by spray.

WARNING: The following references, standards and associated information have been updated at the time of publication, however, it is subject to change without notice at any time.

APPENDIX 1: WORKPLACE EXPOSURE STANDARDS

WES refer to airborne concentration and are divided into three categories:

(a) WES — Time Weighted Average (TWA) — the time weighted average concentration for a normal 8 hour workday or 40 hour workweek, to which nearly all workers may be repeatedly exposed without adverse effects;

(b) WES — Short-Term Exposure Limit (STEL) — the maximal concentration to which workers can be exposed for a period up to 15 minutes provided that no more than four exposures per day are permitted, with at least 1 hour between exposure periods, and provided the daily TWA also is not exceeded; and

(c) WES — Ceiling (WES-C) — the concentration that should not be exceeded even instantaneously.

WES should not be regarded as marking a boundary between safety and danger. Because of a wide variation in personal susceptibility some workers may experience discomfort at levels well below the WES. Therefore, the level of any airborne contaminant should be reduced to the lowest practicable level below the WES.

Isocyanates and their workplace exposure standards 1992.

The Workplace Exposure Standard for all isocyanates including prepolymers is:

WES - TWA 0.02 mg/m^3 (as -NCO)

WES - STEL 0.07 mg/m^3 (as -NCO)

A person who has developed sensitivity to isocyanates should not be exposed to them in any concentration at any time.

APPENDIX 2: SPILLAGE PROCEDURE

1. Put on emergency equipment (see section 8.7.1(b)).
2. Cover spillage with absorbent material such as sawdust.
3. Pour on decontaminant mixture* in a quantity estimated to be twice the volume of the spill.
4. Allow at least 10 minutes for decontaminant to react.
5. Collect all residues from the spillage and place them in an open container.
6. Add further decontaminant mixture to this material, place a loose cover over the container and remove it to a safe place. Discard residues after one day. (See section 8.4).
7. Wash down the area with liquid decontaminant.
8. Rope off the area and post “No Smoking” signs.
9. Clean and decontaminate safety equipment.

* The decontaminant mixture used will depend on the circumstances (see appendix 3). Flammable decontaminant mixtures though more efficient cannot be used close to unprotected electrical equipment. It may also be necessary to use a cold weather decontaminant mixture. A “No Smoking” sign is not necessary with the non-flammable decontaminant mixture.

APPENDIX 3: DECONTAMINATION MIXTURES

1.	***Fast Acting but Flammable Liquid Decontaminant***	
(a)	Industrial Alcohol (denatured ethanol, methylated spirits or isopropyl alcohol)	50% by wt.
(b)	Water	45% by wt.
(c)	Conc. Ammonia Sol. (sg 0.88)	5% by wt.
2.	***Slow Acting Non-Flammable Liquid Decontaminant***	
(a)	Water	90% by vol
(b)	Nonionic Surfactant (100%)	2% by vol
(c)	Conc. Ammonia Solution (sg 0.88)	8% by vol
3.	***Solid Decontaminant***	
(a)	Sawdust	20% by wt.
(b)	Keiselguhr, technical (or china clay or Fuller's earth)	40% by wt.
(c)	Breakdown solution	40% by wt.
	The breakdown solution for the solid decontaminant can be the same as the non-flammable liquid decontaminant above, or as follows:	
(a)	Ethanol	50% by wt.
(b)	Triethanolamine	10% by wt
(c)	Conc. Ammonia Solution (sg 0.88)	10% by wt.
(d)	Water	29.5% by wt.
(e)	Dyestuff (water sol.)	0.5% by wt.
4.	***Cold Weather Decontaminant***	
(a)	Isopropyl Alcohol	50% by wt.
(b)	Perchloroethylene	50% by wt.

APPENDIX 4: SAMPLE HANDOUT SUITABLE FOR TRANSLATION

1. DO wear the protective clothing that your supervisor asks you to wear.
   DO NOT get careless with chemicals.
2. DO move out of the work area quickly if there is a spillage.
   DO NOT attempt to clear the spillage up.
3. DO avoid getting the chemical on your skin or clothes.
   DO NOT ignore splashes on your skin, wash them off at once with soap and water.
4. DO wash yourself when you leave the work area.
   DO NOT keep food or eat or drink in the work area.
5. DO report to your supervisor if you think you can smell the chemical.
   DO NOT ignore a valve that leaks. Report it to your supervisor.
6. DO report to the clinic or your supervisor if your breathing is affected.
   DO NOT neglect splashes in the eye. Wash them out at once and report to your supervisor or clinic.

APPENDIX 5: SPECIMEN WORK PERMIT

Work Permit No: _____ Priority (ABC) Cost Code: _____

Date presented: _____ Time: _____ Date required: _____

Item - Details of work requested or explanation of problems with unit: _____

_____

_____

Estimated man-hours required: _____

Estimated material costs: _____ Total estimated cost: _____

Spare parts required: _____

Approval to proceed given by: _____ Date: _____

CLEARANCE CERTIFICATE

PRECAUTIONS NECESSARY	TICK YES	TICK NO	STEPS TAKEN TO ISOLATE (LONG HAND)	ISOLATED BY	DATE
Electrical isolation	☐	☐			
Chemical isolation: Liquid, vapours, dust	☐	☐			
Steam isolation	☐	☐			
Gas isolation	☐	☐			
Arc welding	☐	☐			
Other	☐	☐			

Protective equipment required: Gloves, spectacles or goggles, respirator, long-distance breather, face shield or chemical hood, apron, footwear, helmet, harness, firefighting, special lighting, stand-by attendant.

Other precautions (state): _____

Precautions necessary checked by: _____ Date: _____ Time: _____

Approval to proceed given by: _____ Date: _____

The above work has been undertaken by the following personnel who have been instructed in the correct safety procedures and work methods to be adopted:

_____ _____

_____ _____

_____ (Signature of person in charge)

Work commenced : Time: _____ Date: _____ *To be completed by engineering supervisor*

Work completed : Time: _____ Date: _____

Materials used: _____ Total man-hours on job: _____

Materials cost: _____

Spare parts used: _____ Spare parts costs: _____

APPENDIX 6: REQUIREMENTS FOR AIR QUALITY (COMPRESSORS OR CYLINDERS) FOR SUPPLIED AIRLINE RESPIRATORS

1. AIR SUPPLY

The necessary capacity of any air service (i.e. compressor) for personal protection shall be calculated on a minimum requirement of 300 litres per minute for the first person and at least 170 litres per minute for each subsequent person.

Air used to supply respirators shall:

(a) have no objectionable odour; and

(b) contain not less than 19.5 percent and not more than 22 percent by volume of oxygen. Additionally, at 15 °C and 100 kPa absolute the air shall:

(i) contain not more than 11 mg/m^3 (10 p.p.m. by volume) of carbon monoxide;

(ii) contain not more than 1400 mg/m^3 (800 p.p.m. by volume) of carbon dioxide;

(iii) contain not more than 1 mg/m^3 (1 p.p.m. by volume) of oil;

(iv) for cylinders, contain not more than 100 mg/m^3 of water when sampled from a cylinder initially filled to a pressure of at least 12 MPa.

1.2 AIR TEMPERATURE

Air supplied from a compressor to a facepiece, hood or helmet should be at a comfortable breathing temperature within the range 15 to 25°C.

1.3 AVOIDANCE OF STALE AIR OR MOISTURE

Arrangements should be made to avoid the pocketing of stale air in pipelines. The use of ring circuits and controlled draining helps to guard against the hazard.

Couplings should be of the “snap type” and should be of different design to those used for other compressed air services.

Provisions should also be made, at appropriate places, to drain away water from any pipeline. Water traps should be drained prior to using the apparatus.

1.4 WARNING DEVICE

Where an ‘in line’ auxiliary (secondary) air supply has not been provided to guard against primary supply failure, the user of an air-supplied respirator shall be warned by an automatic device whenever an inadequacy in the air supply may represent an immediate hazard to the user.

1.5 COMPRESSORS

Systems shall incorporate a receiver of sufficient capacity to reduce pulsations from compressor action and reduce compressor overheating. Compressors shall be well maintained and shall not be allowed to run hot, as harmful substances may be produced by the decomposition of the lubricating oils. Filters should be purged or replaced at regular intervals in accordance with the manufacturer’s instructions. Consideration should also be given to the use of oil-free compressors.

The air intake to the compressors should be sited in an uncontaminated atmosphere. Particular care should be taken to ensure that this requirement is met if portable air compressor is being used to supply breathing air.

The use of filters on any air intake should be of secondary importance when compared with the foregoing requirements.

1.6 GENERAL WORKS AIR SUPPLY SYSTEMS

Where the air supply is used in the manufacturing process as well as in the supply of respirable air, particular care should be taken to avoid the risk of contamination.

Where the air supply is used in the manufacturing process and there is a risk of contamination, the air supply should not be used for personal protection unless it has been filtered to provide the air quality defined in paragraph 1.

In every instance it should be ensured that any back pressures from operating plants using the air supply will not cause contamination of the air used for personal protection.

Provision should be made to ensure that the air lines supplying the breathing apparatus receive a adequate supply of respirable air under all plant operating conditions.

Plant air supplies are not suitable for air-line respirators unless special precautions have been taken for the elimination of scale, rust, water, oil mist, irritating ingredients and odours. It is preferable that a separate installation be provided for respiratory air purposes, and that it be designed to eliminate the above mentioned contaminants.

2. COMPRESSED OXYGEN SUPPLY

Compressed oxygen of the dry breathing type should he odourless and contain not less than 99.5 percent by volume of oxygen.

At 15°C and 100 kPa absolute, it should contain:

(a) less than 11 mg/m^3 (10 p.p.m. by volume) of carbon monoxide; and

(b) less than 1400 mg/m^3 (800 p.p.m. by volume) of carbon dioxide.

APPENDIX 7: MEASUREMENT OF AIR MOVEMENT IN FULL DOWN-DRAUGHT BOOTHS

The procedure to be used for determining the air movement shall be:

1. Divide the booth up into a grid of 9 equal areas.
2. With the booth empty, measure the average downward air velocity 0.5 m below the ceiling filter at the centre of each grid, using a hot wire anemometer. Avoid taking measurements immediately below the filter support frame.
3. No single measurement shall be less than 0.10 m/sec.
4. It is recommended that the average of the 9 grid measurements should be 0.23 m/sec or more. In no circumstances shall the minimum average air movement be less than 0.20 m/sec.

APPENDIX 8: GUIDANCE NOTE ON RECOMMENDED CONSTRUCTION MATERIALS FOR SPRAY BOOTHS

The construction of any spray booth may be varied from the requirements of the Spray Coating Regulations 1962, provided that any alternative construction or lining materials are not ignitable when tested for flammability by AS: 1530 Pt 3: 1989. In addition, the smoke index obtained shall not exceed 5, and the linings must have smooth, easily cleaned surfaces.

APPENDIX 9: RELATED LEGISLATION

Health and Safety in Employment Act 1992 and Regulations — Provide basic occupational safety, health and welfare requirements in factories and undertakings. These include in plant environmental controls to cover such items as ventilation, atmospheric conditions, lighting, noise, and preventative measures for dust explosions.

Other matters covered include protective clothing and equipment, storage of materials, access and egress, provision of amenities such as meal rooms, toilets, and machine guarding.

Factories and Commercial Premises Act (First Aid) Regulations 1985 — Prescribe certain requirements for the provision of first aid kits and their contents, the appointment of persons to administer first aid and the provision of first aid rooms in undertakings employing 100 or more staff.

Spray Coating Regulations 1962 — Require the provision of spray booths and cabinets where spray coating is performed. The regulations specify the construction requirements of spray booths and rooms and also specify ventilation requirements including the discharge of fumes. Requirements for drying ovens, electrostatic spray coating and storage of flammable substances are also included.

Toxic Substances Regulations 1983 — These regulations specify the labelling requirements for containers of TDI and HDI. They are administered by the Public Health Unit at the local Crown Health Enterprise.

Resource Management Act 1991 — Commercial users of isocyanates may be required, under section 15, to obtain a resource consent (discharge permit) for emissions to air, water or land. Users should contact their regional council office for further information (see section 9.4).

Building Act 1991 — Regional council authorities administer the Building Act and other legislative requirements covering items such as building construction, waste disposal, siting of industries, storage of dangerous goods and fire precautions.

RELATED STANDARDS

NZS/AS 1715: 1991. *Selection, use and maintenance of respiratory devices.*
NZS/AS: 1991. *Respiratory protective devices.*

RELATED BOOKLETS AVAILABLE FROM OSH

A Guide to Respirators and Breathing Apparatus.
Guide to the Spray Coating Regulations.
Welding Safety.
How to use Isocyanates Safely (A bulletin for spray painters).