National Occupational Health and Safety Commission

ISOCYANATES

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Foreword

The National Occupational Health and Safety Commission, Worksafe Australia, is a tripartite body established by the Commonwealth Government to develop, facilitate and implement a national approach to occupational health and safety.

The National Commission comprises representatives of the peak employee and employer bodies -the Australian Council of Trade Unions (ACTU) and Confederation of Australian Industry (CAI) - as well as the Commonwealth, State and Territory governments.

Since its establishment, the National Commission has produced occupational health guides. Before the National Commission was established, a series of similar guides was published by the National Health and Medical Research Council.

This Guide has been reviewed and endorsed by a working group of the National Commission as part of the co-ordinated effort by the Commonwealth, State and Territory governments and employee and employer organisations to make Australian workplaces safe and healthy.

Although this Guide has been endorsed by the National Commission, it is an advisory document only. It is produced and distributed in the interests of providing useful information on occupational health and safety for employers, employees and others. This document does not replace statutory requirements under relevant State and Territory legislation.

This Guide is aimed primarily at workers and managers but should also be useful to occupational health and safety personnel and others. It may be used in conjunction with appropriate training and consultation, in line with good management practice.

Contents

Introduction

Isocyanates are compounds containing one or more -N=C=O groups which can combine with other compounds containing alcohol groups. A generic term used to cover all macro-molecular products made by this process is polyurethane. The largest volume use of isocyanates is in the production of polyurethane foams. Isocyanate pre-polymers are included in polyurethane paint formulations which, after curing, form durable films.

This Guide should be read in conjunction with the following Worksafe Australia Guides:

- *Industrial Organic Solvents;*
- *Atmospheric Contaminants*; and
- *Occupational Respiratory Diseases.*

The National Commission publication, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* (latest edition), and Australian Standard AS 2508 *Safe Storage and Handling Information Cards for Hazardous Materials*, should also be consulted.

Reference should be made to the manufacturer's specific product information in the form of a material safety data sheet (MSDS). The MSDS should be updated regularly. The MSDS should conform to the National Commission's recommended format and should be freely accessible to all personnel.

Identification

The most widely used industrial isocyanates and their applications are:

- TDI, toluene di-isocyanate: a liquid, commercially available as a mixture of 2,4 and 2,6 isomers, which is used to produce flexible foams for furniture and car seats;
- MDI, diphenyl methane di-isocyanate: a solid, commercially available in the form of a concentrated solution to produce rigid foams for more solid car parts such as car bumper bars or for thermal insulation;
- HDI, hexamethylene di-isocyanate: a liquid, pre-polymers of which may be used in some paints and lacquers, increasingly for car re-finishing;
- NDI, naphthalene di-isocyanate: a solid which is used in the manufacture of some elastomers;
- MIC, methyl isocyanate: an intermediate in the production of some pesticides;
- wear-resistant polymers as in shoe soles or small wheels;
- pre-polymers for industrial use;
- glues for a range of applications;
- binding agents for moulding sand in foundries; and
- electrical insulating varnishes.

Note: **Where the term 'isocyanates' is used, it refers to all isocyanates.**

Isocyanates are commonly dissolved in aromatic solvents such as xylene and toluene, which in themselves are toxic. For further information, see the Worksafe Australia Guide, *Industrial Organic Solvents.*

In the monomer or pre-polymer forms, TDI and HDI pose a greater health hazard than other commonly used isocyanates. Isocyanates may be heated during use and also may generate heat during reaction, both of which increase vaporisation. Spraying of isocyanates creates aerosols which can also be inhaled.

Many isocyanates are now formulated as pre-polymers by partial reaction with polyols. These compounds are of lower volatility than TDI or HDI and contain less free isocyanate, thus reducing the vapour hazard. The formation of pre-polymers does not substantially reduce the hazard when aerosols are used in spray painting.

Health Hazards

When considering the hazards associated with any workplace, it is essential to understand the relationship between 'hazard', 'exposure', and 'risk'.

'Hazard' is the potential for an agent or process to do harm. 'Risk' is the likelihood that an agent will produce injury or disease under specified conditions.

Health effects can only occur if a worker is actually exposed to the hazard. The risk of injury or disease usually increases with the duration and frequency of exposure to the agent, and the intensity/concentration and toxicity of the agent.

Toxicity refers to the capacity of an agent to produce disease or injury. The evaluation of toxicity takes into account the route of exposure and the actual concentration of an agent in the body.

Exposure routes

The harmful effects of isocyanates follow inhalation of free isocyanate groups in vapour, mists and particles or eye and skin contact with liquid or vapour isocyanate. Because of its inherent toxicity, higher volatility and widespread use, TDI presents the greatest overall hazard, and exposure can occur at all stages of its manufacture and use.

Where TDI and HDI are used as pre-polymers, particularly in polyurethane paints and lacquers, they pose a reduced health risk.

Polyurethane foaming operations rely on the generation of gas, for example, carbon dioxide or halocarbons, which can promote the release of isocyanates as vapour and/or aerosol. Vapour and aerosol release can be expected with volatile isocyanates such as TDI, while aerosols can be expected with less volatile isocyanates and pre-polymers.

Decomposition from welding over polyurethane products and heat removal of insulation varnish may also result in the release of isocyanates. Free isocyanates can be generated when polyurethane foams are cut using hot wire cutting at 300-400°C.

Health effects

Exposure to hazardous material may be acute or chronic. *Acute exposures* generally refer to single dose, high concentration exposures over short periods, while *chronic exposures* involve repeated or continuous exposures over long periods. These exposures may have acute, immediate effects or chronic, long term effects.

Inhalation

In relatively high concentrations, isocyanates have a strong irritant effect on the respiratory tract in most people.

Some people may develop bronchial sensitivity to isocyanates. These people, when later exposed to even very low concentrations of isocyanates, which may be below the exposure standard, may react by developing asthma-like symptoms, such as chest tightness, cough, wheeze and shortness of breath. Such attacks may occur up to several hours after cessation of exposure (for example, during the night) but, if a person is particularly sensitive, the attack may occur earlier.

Asthmatic people are more prone to sensitisation and other adverse reactions. People with a history of asthma should not be exposed to isocyanates (refer to Appendix 1).

Skin

Isocyanates are irritants. Skin sensitisation occurs rarely with TDI, but may be more common in the case of other isocyanates.

Eyes

Isocyanates are irritant to the eyes. Splashes can cause severe chemical conjunctivitis.

Other health effects

Other health effects which have been reported include liver and kidney dysfunction.

Prevention and Control Measures

To establish appropriate prevention of significant health effects, an evaluation of work practices and conditions must be undertaken by qualified health and safety personnel. These practices should be considered an integral part of management's responsibilities. Good occupational hygiene promotes elimination of hazards, where workable. Engineering controls to minimise the hazard at the source, where workable, and administrative controls should be adopted.

The following practices should be adopted to assist in evaluating atmospheric concentrations and minimising the risk to occupational health and safety.

Evaluation

Environmental sampling and analysis should be undertaken at regular intervals by qualified occupational health and safety professionals in accordance with the methods recommended by the appropriate occupational health authority.

The odour thresholds for isocyanates are well above the recommended exposure standards. Special care must therefore be taken in the control of isocyanate hazards because odour cannot be used as an aid in identifying hazardous concentrations.

Monitoring

Monitoring may be used for the evaluation of a hazard and for assessing the effectiveness of control measures. The design and implementation of a monitoring program should be carried out by, or in consultation with, a properly qualified person.

Methods for the determination of atmospheric concentrations of isocyanates range from direct reading instruments for TDI vapour to more complex methods for aerosols of higher molecular weight monomers and pre-polymers. Application of the incorrect method will end in misleading results. The recommendations of the relevant occupational health authority should be followed.

Monitoring of the work environment involves the measurement of atmospheric contaminants at selected locations in the workplace (static, positional monitoring). Personal monitoring involves

the measurement of atmospheric contaminants in the breathing zone of the individual worker.

Personal sampling techniques are preferred for the measurement of individual exposure. Fixed point, static sampling may be used to assess the effectiveness of engineering controls. Under some circumstances, fixed point monitoring can provide an estimate of the potential exposure of a person.

In the control of health hazards due to a specific contaminant, where it has been demonstrated that the exposure of the employee to the contaminant is approaching the relevant exposure standard, *immediate action must be taken to reduce the health hazard* and intensive monitoring should continue. The frequency of sampling should be at least annually, after initial monitoring at the commencement of the process, or following procedural or process changes which may influence exposure patterns.

Records of the results of any monitoring should be maintained and employees should be informed of these results.

Exposure standards

Exposure standards for isocyanates are listed in the National Commission publication, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* (latest edition). Exposure to isocyanates should be reduced to the lowest level workable.

The exposure standards represent airborne concentrations of individual chemical substances which, according to current knowledge, should neither impair the health of, nor cause undue discomfort to, nearly all workers. Additionally, the exposure standards are believed to guard against narcosis or irritation which could precipitate industrial accidents.

Except where modified by consideration of excursion limits, exposure standards apply to long term exposure to a substance over an eight hour day for a normal working week, over an entire working life.

The exposure standards do not represent 'no-effect' levels which guarantee protection to every worker.

Workers should not be exposed to isocyanates at atmospheric concentrations greater than the recommended exposure standards. If workplace levels are kept below these values, people should not develop bronchial sensitisation. However, once sensitisation has occurred, people may develop asthma-like symptoms when exposed to much lower concentrations.

Using personal protective equipment to spray isocyanate - containing paint

Control measures

Where there is a likelihood of worker exposure to isocyanates, *steps should be taken to minimise that exposure*. A thorough examination of work practices is essential. Procedures should be adopted to ensure that workers are not exposed to an extent likely to cause adverse health effects. Control measures include, but are not limited to, the following, which are ranked in priority of their effectiveness:

- elimination/substitution and process modification;
- engineering controls;
- administrative controls; and
- use of personal protective equipment.

Engineering controls

Enclosure

All processes in which isocyanates are used should be enclosed wherever possible. Total enclosure, accompanied by good general ventilation, should be used to keep atmospheric concentrations below the relevant exposure standards.

Local exhaust ventilation

If total enclosure of the process is not feasible, local exhaust ventilation may be necessary. Local exhaust ventilation is essential where TDI or HDI is used or where isocyanate or polyurethane is sprayed. Where other isocyanates or pre-polymers are used and aerosol formation cannot occur, local exhaust ventilation may not be necessary if the atmospheric concentration can be kept below the relevant exposure standards. Where local exhaust ventilation is installed, exhaust vapours should not be vented to the exterior in such a manner as to create a hazard.

Personal protective equipment

In certain circumstances, personal protection of the individual employee is necessary. Personal protective devices should be regarded as being supplementary to substitution and engineering control and should not be used in preference to them as they do nothing to eliminate the hazard.

However, in some situations, minimising exposure to isocyanates by enclosure and ventilation is not possible, particularly during on-site mixing of paints, spray-painting, foaming and maintenance of machine and ventilation systems. In these situations, air-line respirators or self-contained breathing apparatus complying with Australian Standard AS 1716 must be used. The selection, use and maintenance of personal respiratory protective devices should be in accordance with the requirements of Australian Standard AS 1715. Organic vapour respirators with particulate pre-filters and powered, air-purifying respirators are not suitable.

Personal protective equipment must be appropriately selected, individually fitted and workers trained in their correct use and maintenance. Personal protective equipment must be regularly checked and maintained to ensure that the worker is being protected.

Air-line respirators or self-contained breathing apparatus complying with Australian Standard AS 1716 should be used during the clean-up of spills and the repair or clean-up of contaminated equipment and similar situations which cause emergency exposures to hazardous atmospheric concentrations of isocyanate.

Eye and skin contact with isocyanates should be avoided. Particular attention should be given to personal protective equipment being resistant to isocyanates, for example, teflon, viton, nitrile rubber and some PVA gloves. Protective gloves and overalls should be worn as specified in Australian Standard AS 2161. Contaminated garments should be removed promptly and should not be re-used until they have been decontaminated.

Safe storage

Isocyanates should be stored in adequately bunded areas. Nothing else should be kept within the same bunding. Pre-polymers need not be segregated. Drums of isocyanates should be stored under cover, out of direct sunlight, protected from rain, protected from physical damage and well away from moisture, acids and alkalis. Where isocyanates are stored at elevated temperatures to prevent solidifying, adequate controls should be installed to prevent the temperature exceeding 30°C in the case of TDI and precautions against fire should be taken. Where stored in tanks, TDI should be blanketed with a non-reactive gas such as nitrogen. Transfer systems for isocyanates in bulk storage should be fully enclosed and use pump or vacuum systems. Warning signs, in appropriate languages, should be posted where necessary.

Areas in which polyurethane foam products are stored should be supplied with good general ventilation. Residual amounts of unreacted TDI or MDI may be present in the finished foam, resulting in hazardous atmospheric concentrations.

Health assessment

In some occupations, health assessment may form part of a comprehensive occupational health and safety strategy. Where employees are to undergo health assessment, there should be adequate consultation prior to the introduction of any such program. Where medical records are kept, they must be confidential. In some cases, it is valuable to be able to relate employee health and illness data to exposure levels in the workplace. Additional information is given in Appendix 1.

Education and training

All employees working with isocyanates must be informed of the hazards from exposure to the contaminant and the precautions necessary to prevent damage to their health. They should be made aware of the need to carry out their work so that as little contamination as possible is produced, and of the importance of the proper use of all safeguards against exposure to themselves and their fellow workers. Adequate training, both in the proper execution of the task and in the use of all associated engineering controls, as well as of any personal protective equipment, is essential.

Employees exposed to contamination hazards should be educated in the need for, and proper use of, facilities, clothing and equipment and thereby maintain a high standard of personal cleanliness. Special attention should be given to ensuring that all personnel understand instructions, especially newly recruited employees and those with English-language difficulties, where they are known.

MSDS should be obtained for all potentially hazardous substances from the suppliers of such materials before handling.

A management representative should be nominated as responsible for personal protective equipment supply, maintenance and training.

Ensure that all personnel understand the safety procedures associated with the storage and handling of isocyanates. This should include a program on the use and maintenance of respiratory protective equipment.

First Aid

All personnel should be well versed in first aid procedures relevant to the needs of the workplace. Procedures should be laid down after consultation with an occupational health professional. In all workplaces where isocyanates are used, oxygen should be available for emergency use by trained personnel.

Respiratory distress/asthma

If the person is experiencing difficulty in breathing, the following steps should be followed as this condition may develop rapidly into a life-threatening situation:

- Remove the patient from the contaminated area and give them oxygen.
- If breathing has stopped, initiate artificial respiration.
- Seek medical attention urgently.
- If first aid or nursing personnel are present and have received appropriate training, they may administer a bronchodilating drug such as salbutamol by nebuliser. Seek medical attention urgently.

Splashes of isocyanate into eyes

Gently irrigate the eyes with a continuous stream of tepid water for at least 15 minutes. If contact lenses are worn, then irrigate the eyes thoroughly for a few minutes, remove the contact lenses and then continue with further eye irrigation. Refer the patient to a doctor or hospital.

Splashes onto skin

Remove contaminated clothing. Wash skin thoroughly with soap and water. Solvents, for example, methylene chloride, should not be used to remove isocyanates or polyurethane from the skin. Clothing should not be re-used until it has been decontaminated.

Emergency Procedures

Spills and leaks

All personnel should be thoroughly familiar with decontamination procedures to ensure prompt action. Spills of isocyanate, especially of TDI or HDI, represent a very hazardous situation.

The area should be evacuated immediately and specially-trained personnel should deal with the spill. *These people must wear appropriate protective equipment.* The area of the spill or leak should be ventilated. The spill should be neutralised by spreading solid decontaminant over it (see Appendix 2). This should be left for 10 minutes and then collected and placed in a bin which is kept outside and reserved for the purpose. The area should then be thoroughly washed with liquid decontaminant and then thoroughly hosed with water (see Appendix 2).

Decontamination

Isocyanates or isocyanate pre-polymers may be delivered in drums. These drums are designed to be one-way packages and therefore cannot be taken back by the supplier. Isocyanate residues will remain on the walls of depleted drums and therefore the drums must be handled with care. In particular, they should not be cut by equipment which generates heat. Drums which have contained isocyanate should not be re-used or discarded unless they have been decontaminated completely. This should be done as soon as practicable after the drum is emptied. The decontamination should be carried out in a ventilated area taking care to ensure that people are not exposed to isocyanate vapour.

Liquid decontaminant (see Appendix 2) can be used. About 5 - 25L should be put into the drum and the walls well rinsed. This may be done by spraying them with the liquid or by rolling the drum for several minutes. The drum should then be left for 24 hours to ensure complete reaction. *The reaction generates carbon dioxide, so the drum should not be sealed.* The liquid decontaminant may be collected and re-used. Reference should be made to the manufacturer's information.

Disposal of solid and liquid decontaminant should be done in accordance with local authority requirements.

Fire control

Because of their relatively high flash points, the isocyanates present a low fire hazard. However, the polyurethanes, particularly the foams, may burn, releasing di-isocyanate vapour, hydrogen cyanide, pyrolytic products and large quantities of smoke. The exothermic reaction during foam manufacture, if not properly controlled, can lead to a fire. Firefighters tackling polyurethane fires should wear approved self-contained breathing apparatus complying with Australian Standard AS 1716.

Transport

See the Australian Code for the Transport of Dangerous Goods by Road and Rail in the *Commonwealth of Australia Gazette*, No. P 15, 7 April 1987, and Australian Standard AS 2508 for details of transport requirements.

Appendix 1

Additional information

Persons with a history of asthma, atopic conditions, hay fever, recurrent acute bronchitis, interstitial pulmonary fibrosis, pulmonary tuberculosis, occupational chest disease and impaired lung function should be advised against risking exposure to isocyanates.

A person with proven isocyanate sensitivity should not be further exposed to isocyanates.

A significant proportion of people who become sensitised to isocyanate do so in the first two months. A respiratory medical history and/or questionnaire should be conducted and tests of respiratory function should be carried out by appropriately qualified health professionals. This should be done on placement and at periods of two weeks, six weeks and six months after engagement and subsequently at six-monthly intervals. These respiratory function tests should be carried out at the end of the normal shift.

Significant departures from normal values or from baseline levels should lead to reconsideration of workplace exposure and possible job re-allocation.

After absence with respiratory symptoms, the person should be re-examined, including spirometry, to determine if there has been significant departure from previous values.

Appendix 2

Decontaminants for isocyanates

Liquid decontaminant (non-flammable)

Water	by volume	90%
Non-ionic detergent (100%)	by volume	2%
Concentrated ammonia (specific gravity 0.880)	by volume	8%

Solid decontaminant

Sawdust	by weight	20%
Kieselguhr, technical or China clay, or Fuller's earth	by weight	40%
Liquid decontaminant	by weight	40%

Further Reading

Commonwealth of Australia, 'The Australian Code for the Transport of Dangerous Goods by Road and Rail', *Commonwealth of Australia Gazette,* No. P 15, 7 April 1987.

Health and Safety Executive, *Chromic Acid Concentrations in Air*, Document EH 6, Her Majesty's Stationery Office, London, 1977.

Health and Safety Executive, *Isocyanates: Medical Surveillance*, Document MS 8, Her Majesty's Stationery Office, London, 1983.

International Agency for Research on Cancer, *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some Chemicals Used in Plastics and Elastomers*, vol. 39, International Agency for Research on Cancer, Lyon, 1986.

Standards Australia, AS 1716-1984 *Respiratory Protective Devices*, Sydney.

- AS 2161-1978 *Industrial Safety Gloves and Mittens (Excluding Electrical and Medical Gloves)*, Sydney.
- AS 2508-1987 *Safe Storage and Handling Information Cards for Hazardous Materials*, Sydney.

  Card 6.010 *Toluene diisocyanate (TDI).*

  Card 6.012 *Methylene bis (phenylene) diisocyanate (MDI).*