Isocyanates

What Are Isocyanates

Isocyanates are an important family of low molecular weight chemicals. The most common examples are:

- toluene diisocyanate (TDI)
- methylenediphenyl diisocyanate (MDI)
- hexamethylene diisocyanate (HDI)

Other isocyanates used in industry are:

- polymethylene polyphenyl isocyanate (PAPI)
- isophorone diisocyanate (IPDI)
- naphthalene diisocyanate (NDI)

Depending on the type of isocyanate and how it is used, isocyanates may be supplied in solid or liquid forms. TDI, HDI and IPDI are colourless to pale yellow liquids, while NDI is a white powder. MDI may sometimes be supplied in solid form as white or yellow flakes, but is usually in the form of a dark brown viscous liquid.

Isocyanates are formed by mixing amines with phosgenes. An amine is dissolved in a solvent like xylene or monochlorobenzene and mixed with phosgene dissolved in the same solvent for several hours at high heat. At the end of the reaction, fractions of isocyanate, phosgene, hydrochloric acid, excess solvent and waste residues are the result.

Representative Trade Names of Isocyanates (See Reference # 6)			
Centari	Desmodur	Hylene	Imron
Isonate	Mondur	Macconate	Niax
Rubinate			

How Are Isocyanates Used

TDI is a combination of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate. TDI is usually found in an 80:20 mixture of these two forms. TDI is used in the manufacture of flexible foam used in a variety of products, including:

- mattresses
- upholstery cushions
- automobile seats
- packaging materials

MDI has replaced TDI in the production of rigid foams because it is less hazardous due to its lower volatility (its ability to produce a vapour). Rigid foam is used as insulation in home refrigerators and ovens, while spray-in foam is used for railroad cars, truck trailers, and boats. MDI is used as part of a no-bake binder system for casting moulds in foundries.

As protective coatings, polyurethanes are applied to electrical wiring because they are good insulators. They are used as two-part paints and floor, concrete and wood finishes where their hardness and durability are important. Aircraft, truck and other coatings are often composed of diisocyanate prepolymer systems. Isocyanates are also used as adhesives and elastomers in automobile bumpers, printing rolls, liners for mine and grain elevator chutes, shoe soles, coated fabrics, and spandex fibres.

When making polyurethane foams, isocyanate (part A) is usually added to polyether or polyester polyols (part B or resin) along with fire-retarding agents, catalysts and blowing agents (part B) to form polyurethane. Adding water creates carbon dioxide gas followed by foam production. If water is not added, the polyurethane mixture can be used as a coating material.

Commercially, polyurethane adhesives and coatings may be available as two-component systems that react together and must be mixed just prior to use or as one-component systems that require reaction with oxygen or moisture after application for curing.

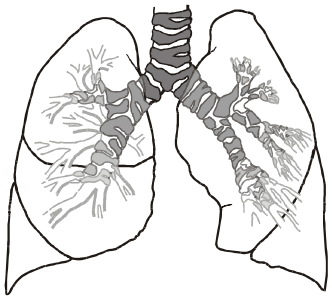
Occupational Exposures (See Reference #6)		
adhesive workers	isocyanate workers	polyurethane foam makers
aircraft builders	lacquer workers	rubber workers
appliance makers	life preserver makers	ship builders
boat makers	mine tunnel coaters	ship welders
cushion makers	painters	textile processors
foam makers	plastic foam makers	upholstery workers
insulation workers	plastic moulders	varnishers
		wire-coating workers

What Are The Health Effects Of Isocyanates

Because isocyanates are highly reactive, exposure can result in primary irritation, sensitization and hypersensitivity reactions (allergic reactions). The breathing system, the eyes and the skin are the main areas affected by exposure.

It is also important to consider the additives or solvents used in the production of polyurethane. Catalysts such as metal salts (for example, organotin compounds) or tertiary amines may be used. Combustion-retarding agents and blowing agents may also be added to the preparation and are usually organic phosphates or phosphonates and may contain chlorine or bromine. Methylene chloride or chlorofluorocarbons have been used as blowing agents in the manufacture of polyurethane foam.

Breathing System Effects Adverse effects to the breathing system associated with isocyanate exposure include acute (short-term) or chronic (long-lasting) effects due to a single overexposure, chronic breathing problems caused by long-term low level exposure, occupational asthma and hypersensitivity pneumonitis (allergic reaction of the lungs).



Respiratory Diseases Associated with Isocyanates (See Reference #7)
Direct irritation of the respiratory tract
Asthma
Chronic obstructive pulmonary disease
Hypersensitivity pneumonitis (allergic inflammation of the lungs)
Pulmonary disease-anemia syndrome (hemorrhagic pneumonitis (bleeding in the lungs))

The major concern with isocyanate exposure and the breathing system is asthma (refer to OHCOW Information Bulletin on *Occupational Asthma*). Typically, asthma begins near the end of the work day, continues through the night improving somewhat in the morning hours, and happening in the same pattern the next day.

Sensitized workers have reported symptoms at extremely low levels of exposure (1 part per billion (ppb)). Although asthma medication may control or prevent symptoms in these workers, a fatal attack of asthma may unexpectedly occur. Also, medication may not alter the natural history of asthma, and continued exposure to isocyanates may lead to more severe and prolonged disease that may generalize to other agents. Even after exposure stops, respiratory symptoms may continue for years.

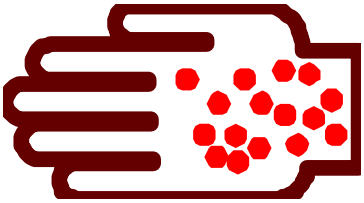
Scientific studies of TDI-exposed workers show that 5% to 20% of workers exposed to TDI may become sensitized to the chemical, although values of up to 30% have been reported depending on exposure levels and criteria used to define sensitivity. There seems to be no relationship between a history of allergy or atopy (genetic link) and the development of isocyanate-induced asthma.

Varying periods of isocyanate exposure (months to years) may exist before asthma develops. Although it has been suggested that the development of isocyanate-induced asthma requires about 2 years of exposure to develop, the latency period is so unpredictable that such generalizations are difficult to make.

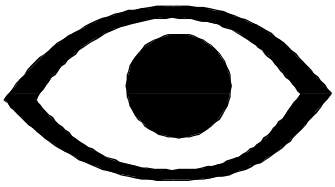
Clinical Features of Isocyanate-Induced Asthma (See Reference #1)
1. Typically, there is no history of pre-existing asthma. 2. Worker is exposed to isocyanates. 3. Recurrent asthma occurs in relation to the workplace. 4. Most often, there is improvement away from the workplace. 5. Once the worker is sensitized, episodes of asthma recur following exposure to subirritant levels of isocyanates. 6. In chronic cases, recurrent asthma can develop with exposure to non-specific irritants unrelated to isocyanates and away from the workplace.

Smoking and TDI effects on lung function were found not to be additive.

Skin Effects Direct skin contact with isocyanates may cause skin irritation, rashes, blistering and reddening. The scientific literature indicates that it is possible to produce "allergic skin sensitization" of guinea pigs and mice with

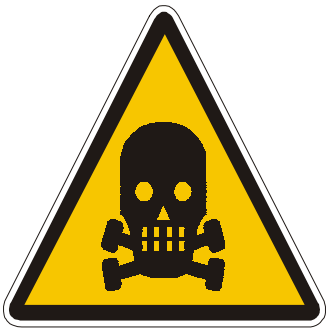


solutions of TDI. Skin contact with TDI may result in respiratory tract hypersensitivity, as has been shown in guinea pigs.



Eyes Exposure to airborne isocyanates may cause the eyes to tear and result in eye irritation and a temporary decrease in sharpness of vision. Isocyanates splashed into the eye can cause severe irritation and possible damage to the cornea (the membrane covering the lens of the eye).

Nervous System Effects Symptoms resulting in nervous system effects include a feeling of drunkenness, numbness and loss of balance . These have been described as occurring immediately after a single severe exposure to TDI by firefighters in a burning polyurethane foam factory, with some symptoms lasting up to 4 years. They also reported nausea, vomiting and abdominal pain, which were temporary symptoms.



Cancer The International Agency for Research on Cancer (IARC) determined there is sufficient evidence for carcinogenicity of TDI to experimental animals but inadequate evidence to determine its cancer-causing effects in humans. However, in the absence of adequate data in humans, it is reasonable to regard chemicals for which there is sufficient evidence of carcinogenicity in animals as if they represented a cancer risk to humans. NIOSH has released information classifying TDI as a potential occupational carcinogen.

Reproductive Effects There is limited evidence that exposure to toluene-2,4-diisocyanate may cause temporary impotence in males.

How Can Workers Be Exposed To Isocyanates

Workers can be exposed to isocyanates thorough inhalation or by direct contact.

Inhalation Isocyanates may be inhaled if they are present in the air in the form of a ***vapour, mist or dust.***

- A **vapour** is the gaseous form of a substance that has been given off (evaporated) from a liquid or a solid. The amount of isocyanate vapour released into the air in a given time depends on temperature and volatility of the specific isocyanate used. The higher the temperature to which the isocyanate is heated, the more rapidly the vapour will be released.
- A **mist** is a suspension of small liquid droplets in air. Mists are formed in the workplace by operations that involve spraying, such as spray painting or the application of spray-on insulation.
- A **dust** is a suspension of solid particles in air. Some isocyanates, such as MDI, are sometimes supplied in flake or powder form, which can give rise to a dust hazard. Exposure to isocyanate dust may also occur as a result of sawing or scraping of uncured polyurethane that still contains some unreacted isocyanate groups.

Since the odour is only detectable at over 100 times the allowable limit, smell is not an acceptable means to detect exposure.

Skin and eye contact Isocyanate vapour may cause irritation of the eyes, nose and throat. Liquid isocyanates can cause damage if they come in contact with the skin or eyes. Isocyanates are not abosorbed into the body through the intact skin.

Safety And Fire Hazards Of Isocyanates

When isocyanates react with water, ammonia, alcohols or strong bases, heat and carbon dioxide gas are released. If such a reaction occurs in a sealed container, the container may explode, releasing isocyanate vapour and other toxic gases. Isocyanates are not considered to be highly combustible. However, in the presence of fire and high heat, they will burn and release toxic gases such as carbon monoxide, nitrogen oxides and hydrogen cyanide. Finished polyurethane products are more combustible than isocyanates and, when burned, can release a number of hazardous substances.

Air Monitoring

Airborne TDI monomer (one unit in a polymer) exists primarily as a vapour while MDI monomer can be either a vapour, an aerosol, or a combination of the two. The

polymeric, prepolymeric, modified or partially polymerized isocyanates will exist primarily as aerosols, not vapours, due to their higher molecular weights. These aerosols may or may not be receptive to sampling, analysis or monitoring by the same techniques as free TDI or MDI monomer.

Over the past 30 years many advances have been made in the sampling and analysis of airborne isocyanates. The primary focus during this period was in the sampling and analysis of monomeric isocyanates. However, more recently several investigators have turned their attention to measuring the total reactive isocyanate groups (TRIG) in the air. The TRIGs in the air will come from the monomers and the polymeric, prepolymeric or partially reacted isocyanate materials. The current state-of-the-art technology leaves several unanswered questions about identification and analysis of polymeric isocyanates and TRIGs.

Air levels of TDI can be measured by a variety of methods. The Marcali method and its derivatives, also called wet colourimetric methods, are the oldest and have been the reference for newer methods. It is still the reference method for some organizations. This method uses an impinger with a solution of either hydrochloric acid and acetic acids for sample collection, and N-1-naphthylethylenediamine for colourimetric analysis of the impinger solution in the laboratory. It is designated as NIOSH Methods 141 and 142. With this method there is a positive interference from aromatic amines. This is important in any case where aromatic amines may be present in the air. Also, it cannot identify specific isocyanates. This is not a problem when only a single isocyanate is present.

For the most part the Marcali method is not used presently to measure MDI. Exposure data reported in any study in which the Marcali method was used to measure MDI concentrations must be evaluated with caution.

The Regulation respecting Isocyanates (Ontario Regulation 842/90, as amended by Ont. Reg. 377/91 and 518/92) requires that the Marcali method be used to measure MDI and TDI concentrations when they are the only isocyanates present in the workplace.

Tape methods or dry colourimetric methods are based on colour-forming reactions that occur when chemically prepared paper is exposed to air containing isocyanates. After monitoring, the tape is passed through a meter to measure the quantity present. Many dry tape instruments cannot identify specific isocyanates or are subject to interference from other substances.

Chromatographic methods (gas chromatography, thin layer chromatography and high performance liquid chromatography [HPLC]) are the most sensitive for measuring and distinguishing between isocyanates but are technically difficult and expensive.

Other Methods:

1. NIOSH Method 2535

☞ uses nitro reagent (p-nitrobenzyl-N-n-propylamine) deposited on glass wool and packed in a sampling tube

☞ this method has seen little use in recent years for aromatic isocyanates

☞ good mainly for vapours

☞ nitro reagent is good for a maximum of 10 days after preparation, as long as it is kept in the dark; tubes should be wrapped with black tape to keep out light

☞ uses HPLC analysis

2. NIOSH Method 5505

☞ uses MOPP [1-(2-methoxyphenyl)piperazine] in an impinger

☞ uses HPLC analysis

☞ since the total amount is determined by comparing the difference between the original amount of MOPP and the final lesser amount, there is a significant degree of uncertainty in measuring a small difference between two large quantitities

☞ health effects studies using this method should not be considered to have quantitative exposure results

☞ this method was formally retracted by NIOSH

3. NIOSH Method 5521

☞ uses MOPP in an impinger for sampling with HPLC analysis

☞ since measuring the amount of isocyanate is by direct analysis of the derivative rather than by calculation of the difference between the two numbers, this method eliminated some of the limitations seen with Method 5505

The Regulation respecting Isocyanates (Ontario Regulation 842/90 as amended by Ont. Reg. 377/91 and 518/92) requires that a modified version of NIOSH method 2535 be used to measure HDI, IPDI and mixtures of isocyanates. While more expensive, it is a superior method for measurement of MDI or TDI alone.

Reviewing and clarifying the limitations of these techniques addresses questions of sampling and analytical efficiency at very low levels, which often are below the levels thought to cause health effects. It is important to understand these limitations when reviewing health effects studies that used sampling and analytical methods that through experience have been shown to give potentially inaccurate results.

In recognition of these limitations, investigators have called for future research efforts focusing on a number of topics for sampling and analysis methods.

Workplace Controls And Practices

Unless a less toxic chemical can be substituted for a hazardous substance, engineering controls are the most effective way of reducing exposure. The best protection is to enclose operations and/or provide local exhaust ventilation at the site of isocyanate release. Isolating operations can also reduce exposure. Using respirators or protective equipment is less effective than engineering controls but is sometimes necessary.

In evaluating the controls present in your workplace, consider:

- how hazardous the substance is
- how much of the substance is released into the workplace
- whether harmful skin or eye contact could occur

- Where possible, automatically pump liquid isocyanates from drums or other storage containers to process containers.
- If isocyanates must be used, use those which have fewer “free” isocyanates or those that are less volatile.

- Protective clothing, including splash-proof chemical safety goggles and face shield, rubber gloves and coveralls, should be worn by workers handling isocyanates. Because isocyanates can cause rubber to become brittle and crack, care must be taken to replace damaged protective equipment. Butyl rubber, butyl nitrile or natural rubber are cited in the literature.
- All protective clothing (suits, gloves, footwear, headgear) should be clean, available each day and put on before work.
- Any clothing or protective equipment that becomes contaminated with isocyanates should be decontaminated before it is reused. A solution of nine parts water, one part ammonia and some liquid detergent can be used for soaking contaminated clothing.
- The employer must take responsibility for cleaning contaminated clothing and for ensuring that laundry workers are aware of the hazards of cleaning isocyanate-contaminated clothing.
- Do not take contaminated work clothes home. Family members could be exposed.
- Eyewash fountains should be provided in the immediate work area for emergency use.
- On skin contact, immediately wash or shower to remove the chemical.
- Do not eat, smoke or drink where isocyanates are handled, processed or stored, since the chemical can be swallowed. Wash hands carefully before eating, drinking, smoking or going to the washroom.
- Where the potential exists for overexposure to isocyanates, a NIOSH-approved supplied-air respirator with a full facepiece operated in a pressure-demand or other positive-pressure mode should be used. For increased protection use in combination with an auxilliary self-contained breathing apparatus operated in a pressure-demand or other positive-pressure mode.
- Exposure to 2.5 ppm is immediately dangerous to life and health (IDLH). If the possibility of exposure above 2.5 ppm exists, use a NIOSH-approved self-contained breathing apparatus with a full facepiece operated in a pressure-demand or other positive-pressure mode.
- Respiratory equipment should only be used if the employer has a written program that takes into account workplace conditions, requirements for worker training, respirator fit testing and medical exams.

- Emergency protective equipment should be readily available for use in the event of spills. This should include respirators, long-sleeved impervious gloves, full waterproof clothing, rubber boots and head protection.
- First aid procedures for dealing with splashes and accidental ingestion of isocyanates should be posted in accessible locations.
- Post hazard and warning information in the work area. In addition, there should be an ongoing education and training effort in place on all information on the health and safety hazards of isocyanates.
- Medical surveillance must be provided by the employer according to the requirements of the Designated Substance Regulation for Isocyanates.

The Ontario Ministry of Labour has issued an alert entitled *Spraying of Polyurethane Foam Insulation on Construction Projects.* This alert should also be referred to since it outlines precautionary measures for spraying polyurethane foam on residential and commercial construction projects.

Exposure Limits

Organization	Exposure Limit
Ontario Ministry of Labour	0.005 ppm [TWA] (TDI, MDI, HDI, IPDI)
American Conference of Governmental Industrial Hygienists (ACGIH)	0.005 ppm [TLV] (TDI) 0.02 ppm [STEL] (TDI)
Occupational Safety & Health Administration (OSHA)	0.005 ppm [PEL] (TDI) 0.02 ppm [Ceiling] (TDI)
National Institute for Occupational Safety & Health	treated as a potential carcinogen, therefore, occupational exposures to carcinogens should be limited to the lowest feasible concentration 2.5 ppm [IDLH]

Special Note

Because isocyanates have been designated in Ontario, all workplaces containing isocyanates must be assessed and control programs set up through consultation with the Joint Health & Safety Committee (JHSC). Refer to the Ministry of Labour's

Occupational Health & Safety Act (Isocyanates - Designated Substance Regulations, R.R.O. 1990, Reg. 842 [as amended by O. Reg. 377/91; and 518/92]).

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4. NIOSH. Pocket Guide to Chemical Hazards. June, 1994.
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6. Phillips KK; Peters JM. 94. Isocyanates. In: *Hazardous Materials Toxicology - Clinical Principles of Environmental Health*. Editors: John B. Sullivan, Jr, MD and Gary R. Krieger, MD, MPH, DABT. Williams & Wilkins, 1992.
7. Rosenstock L; Cullen MR. Section Four: Hazards in the Workplace and the Environment. *Textbook of Clinical Occupational & Environmental Medicine*. W.B. Saunders Company, 1994.

If workers are suffering symptoms from isocyanate exposures they should see a doctor and inform the Joint Health & Safety Committee.

The Occupational Health Clinics for Ontario Workers Inc. can assist in medical and occupational hygiene evaluations for isocyanates.

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