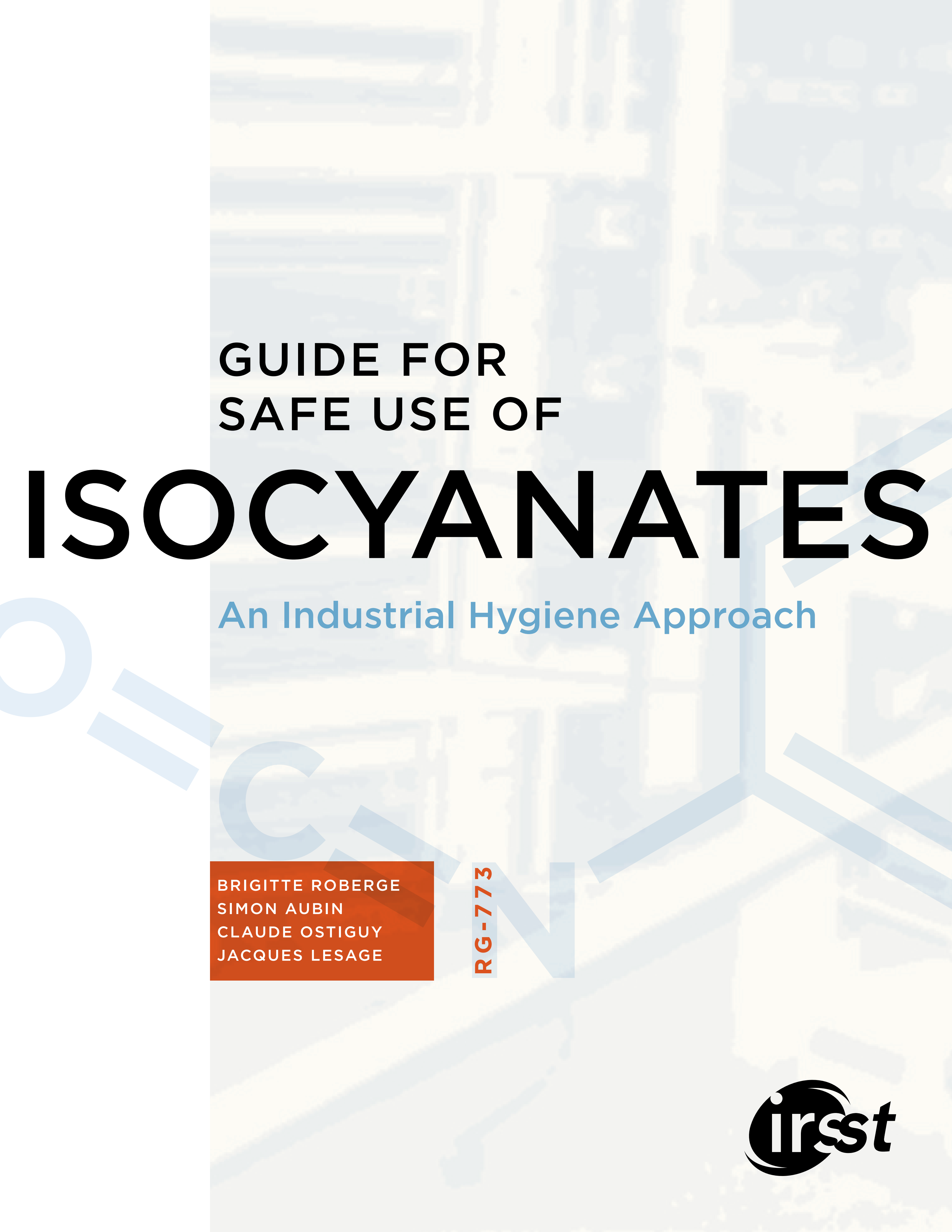

GUIDE FOR SAFE USE OF
ISOCYANATES

An Industrial Hygiene Approach

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RG-773

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The Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST), established in Québec since 1980, is a scientific research organization well-known for the quality of its work and the expertise of its personnel.

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FOREWORD

Isocyanates can be harmful to the skin and the respiratory system. They are in fact the main cause of occupational asthma (OA) in Québec. Like the original version, this edition of the *Guide for Safe Use of Isocyanates – An Industrial Hygiene Approach* is intended for employers and workers in Québec as well as anyone working in the field of occupational health and safety. It is designed to educate, inform and raise awareness, and has no regulatory value. Readers will come to understand the chemical hazards associated with isocyanates and will be able to make informed decisions about ways to reduce exposure and possibly the incidence of occupational asthma. This guide is not a substitute for the information contained in Material Safety Data Sheets.

Because this guide is widely used, an update was justified. This version therefore contains current data and discussions of the risks inherent in inhalation exposure (respiratory hazard) and dermal exposure (cutaneous hazard). Other hazards are present in the workplace: for example, safety hazards, fire and explosion hazards, and ergonomic hazards. Though these and other chemical hazards linked to contaminants in the products used (such as solvents) are not discussed in this document, it is nonetheless important that they be considered in any comprehensive risk analysis.

This second edition is presented according to the industrial hygiene approach, a framework for managing health risks by anticipating, recognizing, evaluating, controlling and communicating the risk factors linked to exposure to chemicals (such as isocyanates) or to biological or physical agents. The approach adopted in this guide is that of hygiene rather than risk analysis.

This update contains several new features, such as a case studies chapter to help the reader understand exposure and how it can be dealt with. We have also added a short summary in bold lettering at the beginning of each chapter. Links lead to chapters or sections dealing more specifically with a given aspect, while hyperlinks (in blue in the text) take the reader to related Web sites. At the end of the document is a list of all these hyperlinks, which were functional at the time of printing (Appendix 3). We have also provided a glossary (including abbreviations) in Appendix 2.

ANTICIPATION

1

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ANTICIPATION

In an industrial hygiene approach, the preparatory stages – anticipation and recognition – are for collecting relevant data on the chemicals in the mixtures used and on the intermediate and final products in the process, including the physical nature of the substances. Data on the toxicity of each substance identified and their reference values are also collected. The data gathering is facilitated by consultation of the material safety data sheets (MSDS) and other sources. In addition, data on the workplace (environmental assessment) is collected, mainly from the literature and from records of previous sampling campaigns.

Using the scientific knowledge available and the expertise acquired in other situations, it is possible to anticipate the hazards associated with a process or the use of a chemical substance. Once a hazard has been identified, the risk must be anticipated. The Canadian Centre for Occupational Health and Safety defines a risk as "the chance or probability that a person will be harmed or experience an adverse health effect if exposed to a hazard." (CCOHS, 2009).

Still today, assessing exposure to isocyanates is a challenge, for several reasons: the wide variety of chemicals used, regulation limited to only a small fraction of them, and exposure to them in the form of aerosols or vapours, depending on the process and on the physical and chemical properties of the substances. This risk is already very complex, but there is the added risk of exposure due to thermal degradation of these polymers and to residual quantities of unreacted isocyanates in the finished product.

Isocyanates are organic chemical substances characterized by the presence of one or more reactive isocyanate groups (NCO), or functional groups, attached to an organic radical. They can be categorized according to the number of isocyanate groups (NCO) attached to the organic radical. As a result, we have monoisocyanates, diisocyanates, triisocyanates, etc. The nature of the organic radical may be aromatic, aliphatic or alicyclic. These substances can be grouped into three families according to the number of isocyanate functional groups: monoisocyanates, which contain only one isocyanate group, are rarely used in Québec, and among these only methyl isocyanate is regulated; diisocyanates (two NCO isocyanate functional groups), which constitute the smallest base unit allowing polymerization, are regulated; oligomers (also called polyisocyanates, prepolymers or homopolymers) are generally composed of a mix of isomers of molecules containing two or more isocyanate groups. The commercial products used in numerous processes are generally made up of diisocyanates and oligomers. Note that in this document, the term "isocyanate" will be used to designate any compound having at least one isocyanate group.

Vapour pressure is very useful for estimating the maximum concentration of vapourized isocyanates in the air at the saturation point, as well as the physical form that these substances will take in the air when the process is implemented (in the form of vapour or aerosol).

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Table 1.1 shows the main isocyanate molecules likely to be present during processes, along with their vapour pressure and saturation concentration at 20°C in air. An increase in temperature will lead to an increase in vapour pressure.

TABLE 1.1

PHYSICAL AND CHEMICAL PROPERTIES OF ISOCYANATES

NAME OF ISOCYANATE (ABBREVIATION)	CAS*	VAPOUR PRESSURE (mm Hg at 20°C)	SATURATION CONCENTRATION IN AIR (ppm)
Methyl isocyanate (MIC)	624-83-9	390	510,000
Butyl isocyanate (nBIC)	111-36-4	16	21,000
Phenyl isocyanate (PhIC)	103-71-9	2	2,600
Hexamethylene diisocyanate (HDI monomer)	822-06-0	0.025	33
Hexamethylene diisocyanate (HDI polyisomer)	28679-16-5	7.5×10^{-5}	0.099
Toluene-2,4 diisocyanate (2,4-TDI)	584-84-9	0.02	33
Toluene diisocyanate (80:20 mix of isomers) (TDI)	26471-62-5	0.02	33
Isophorone diisocyanate (IPDI)	4098-71-9	5×10^{-4}	0.66
Diphenylmethane-4,4' diisocyanate (MDI)	101-68-8	$< 1 \times 10^{-5}$	< 0.013
Prepolymer diphenylmethane-4,4' diisocyanate (PMDI)	9016-87-9	$< 1 \times 10^{-5}$	< 0.013
Dicyclohexylmethane diisocyanate-4,4' (HMDI)	5124-30-1	1×10^{-5}	0.013

* CAS: CAS (Chemical Abstracts Service) registry number

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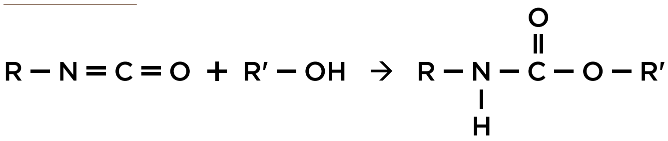
ANTICIPATION

Isocyanates react rapidly with a wide range of organic substances having a labile (unstable) proton. The polymerization reaction is characterized by an attack on the double nitrogen-carbon bond of the isocyanate group (-N=C=O), followed by addition of a copolymer. The reaction therefore involves a copolymer having an acidic hydrogen. Most commonly, isocyanates react with substances having an alcohol function (OH) to form a urethane (Equation 1).

EQUATION 1

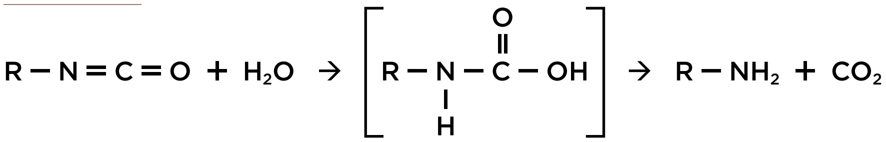


$$R-N=C=O + R'-OH \rightarrow R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R'$$

Polymerization can thus occur between a diisocyanate or polyisocyanate and a diol or polyol to produce a polyurethane. The type of alcohol – linear or branched – will determine the properties of the desired polymer. This kind of polymerization is commonly used in the production of rigid and semi-rigid foam, elastomers, covering materials and vehicle coatings[1] (primers, hardeners…).

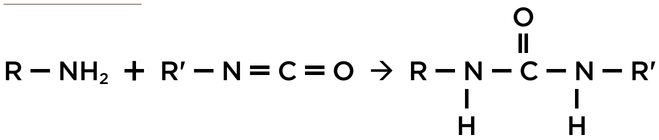
Isocyanates hydrolyze slowly to form amines, which react quickly with another isocyanate group to produce a urea derivative and CO_2 (Equations 2, 3, 4). However, isocyanates do not react with ambient humidity.

EQUATION 2



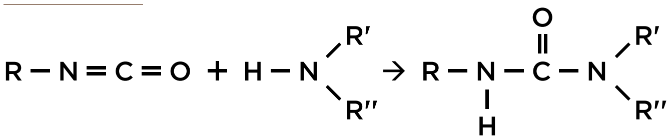
$$R-N=C=O + H_2O \rightarrow \left[R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-OH\right] \rightarrow R-NH_2 + CO_2$$

EQUATION 3



$$R-NH_2 + R'-N=C=O \rightarrow R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R'$$

EQUATION 4



$$R-N=C=O + H-N\begin{matrix}\diagup R' \\ \diagdown R''\end{matrix} \rightarrow R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-N\begin{matrix}\diagup R' \\ \diagdown R''\end{matrix}$$

As seen in Equations 3 and 4, isocyanates react with primary or secondary amines having a labile proton to form urea derivatives. Amines are used as a catalyst in certain processes. Many analytical methods use secondary amines to stabilize isocyanates during sampling for laboratory analysis (see Sampling and analysis).

---

[1] In this document, "coating" includes primers, paints, hardeners and other products, especially those applied to vehicles.

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ANTICIPATION

Isocyanate-based products containing a mix of a monomer and various oligomers and isomers are often used as binders or to form polyurethane compounds in the presence of polyols and different additives as well as in certain applications involving solvents. They are very widely used in industrial applications such as injection moulding and the manufacture of low- and high-density flexible foam and sprayed polyurethane rigid foam. Isocyanates are also used to produce the polyurethane elastomers employed by the automotive industry and in engineering. Their uses range from wood composite binding agents to the reactive material used to make orthopedic plaster casts, and from the manufacture of adhesives, coatings and lacquers to rubber vulcanization.

> As a rule, MSDSs list the substances (such as isocyanates) present in the product they are describing. However, the information about chemical composition is not always true to reality. Depending on the regulations in the country where the MSDS was written, it might not disclose the presence of an isocyanate and could thus be misleading for the person consulting it. Moreover, the user must not look solely for the presence of isocyanate monomers (generally the only chemical form of isocyanate having a reference value, or RV). The presence of isocyanates in polymer or oligomer form – found in increasing proportions in commercial products – requires the user to follow the same steps for prevention of isocyanate-related health hazards.

1.1 MOST COMMON ISOCYANATES

Toluene diisocyanate (isomer mixture) (**TDI**)

This mixture of isomers of 2,4-TDI and 2,6-TDI in a ratio of 80:20 is most often used to manufacture polyurethane flexible foam. Another use, though less common, is in the production of varnish.

Diphenylmethane-4,4′ diisocyanate (**MDI**)

MDI is marketed in the form of an oily liquid made of a mixture of monomer and oligomer isomers, a prepolymer of polymeric MDI, or PMDI. The most common monomer/oligomer ratio is about 50:50; however, for certain processes, the monomer content may range from 25% to 75%. MDI is used in the manufacture of polyurethane rigid structural foam, elastomers, wood composite binding agents, casting molds and certain types of glue.

Hexamethylene diisocyanate (**HDI**)

Commercial HDI, frequently used as a reactive agent in coatings and paints, is almost entirely composed of HDI oligomers (biuret and isocyanurate); the HDI monomer content is often below 1%. HDI is basically used in vehicle coatings (primers, paints, hardeners, etc.) and in polyurethane varnishes and coatings. Since application is often through spraying, a high proportion of HDI oligomers in air samples can be expected. HDI-based urethanes are resistant to ultraviolet (UV) rays and fluctuations in temperature.

Isophorone diisocyanate (**IPDI**)

IPDI is present in certain mixtures in the form of isomers. It is an isocyanate with an alicyclic structure that can be used to make polyurethanes. Like HDI, it is UV-resistant. It is used in the manufacture of vehicle coatings – often in combination with HDI – and elastomers.

Table 1.2 shows the range of common applications for isocyanates.

TABLE 1.2

RANGE OF PRODUCTS ACCORDING TO POLYMER DENSITY AND RIGIDITY

POLYMER DENSITY/RIGIDITY	PRODUCT DESCRIPTION	SUBSTANCES
	FLEXIBLE FOAM	
⊖	Block	TDI, PMDI
	Moulded	TDI, PMDI
	RIGID FOAM	
	Flow casting	PMDI, TDI
	Blocks and panels	PMDI
	Spray	PMDI
	RIGID STRUCTURAL FOAM	PMDI
	BINDERS	PMDI, TDI
	ELASTOMER	
	Injection casting	MDI, PMDI
	Elastomer casting	MDI, TDI, HMDI, prepolymer
	COATINGS (PAINT)	
⊕	Flexible coating	PMDI
	Primer (single-pack)	HDI, TDI, IPDI
	Sealants and waterproofing products	HDI, TDI, IPDI
	Topcoats (two-pack)	HDI, TDI, IPDI

1.2 ANTICIPATION OF THE PHYSICAL NATURE OF AIRBORNE ISOCYANATES

Because of the wide range of isocyanates present in industry, and because their physical and chemical properties and the polymerization processes are so diverse, environmental assessment of exposure remains a challenge; hence the importance of an approach starting with anticipation (gathering of information on isocyanates) and ending with the implementation of controls and of means for evaluating the efficiency of those controls.

In all cases, anticipation of the physical form of airborne isocyanates contributes to a full evaluation and implementation of effective control measures.

As indicated by their vapour pressures (Table 1.1), diisocyanates are not highly volatile. HDI and TDI monomers are often present in workplaces in the form of vapour at ambient temperatures. Increased temperature leads to an increase in vapour pressure and in the concentration of these substances in the vapour phase. Spraying promotes the evaporation of isocyanates by significantly increasing contact with air. However, for processes using MDI and HDI oligomers, these substances will mainly be present in the air as aerosols even if the application process involves spraying of the product or the production of airborne dust.

1.3 ANTICIPATION OF ISOCYANATES FROM THERMAL DEGRADATION

In addition to the risk of overexposure to isocyanates during application of polymerization processes, the literature also reports the possibility of low-level exposure to isocyanates when polyurethane products are subjected to enough heat to degrade them.

“Thermal degradation” refers to the secondary products emitted during pyrolysis or combustion. “Pyrolysis” means the degradation of a product under the effect of heat, while “combustion” means the same but in the presence of oxygen.

Certain kinds of work requiring the use of heat on or near polyurethanes may lead to a degradation of the product, which will release isocyanates into the air. For example:

- Welding
- Heating of polyurethane foam
- Glue heating
- Cutting with a torch or hot wire
- Cutting with a hot chisel
- Crushing
- Sawing
- Grinding

The thermal stability of polyurethanes varies greatly with their structure. Degradation has been observed at temperatures as low as 150°C. It is important to be aware of this potential exposure risk, because in situations where there is no smoke or flame, there are very few visible clues to alert the worker to the presence of isocyanates.

1.4 ANTICIPATION OF ISOCYANATES IN FINISHED PRODUCTS

Another potential source of exposure to isocyanates is the presence of unreacted isocyanates in finished products. Many laboratory studies have demonstrated the presence of isocyanates such as unreacted TDI in flexible foam and unreacted MDI in semi-rigid foam. There is no evidence of dermal exposure following contact with a finished product, nor of exposure to airborne isocyanates following a potentially low emission of these substances in vapour phase. Research is still under way on these topics.

To conclude this section, the sampling methods must be adapted to the physical nature of the isocyanates present, i.e., vapours and aerosols, both of which are often found in the same environment and are generated by the same process. An isocyanate evaluation should lead to the introduction of methods of control to reduce or even eliminate exposure.

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RECOGNITION

2

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RECOGNITION

In the anticipation stage, potential exposure from use of isocyanates is documented according to their physical nature and other factors. The recognition stage provides other relevant information (effects on health, regulation of use, etc.) that can be used to develop a sampling and analysis strategy for making a quantitative assessment of exposure – an essential element in determining the prevention measures to put into place.

2.1 EFFECTS ON HEALTH

Isocyanates are powerful skin and respiratory tract irritants and sensitizers. They can cause various types of illness in the lungs, the most severe being occupational asthma (OA), which can manifest after several months or years of exposure. The symptoms often appear in the evening, so that one does not immediately make the connection between work and the discomfort one is feeling. Even today, isocyanates are the leading cause of OA in most industrialized countries, and all isocyanate functional groups, whether monomer or oligomer, contribute to the disease. Once a worker has OA, he or she can no longer be exposed to isocyanates, since they could trigger an asthmatic reaction even at concentrations much lower than the permissible exposure value. Moreover, the worker could suffer from exacerbated asthma in the presence of other lung irritants.

In Québec, the Réseau de référence pour l'asthme professionnel (RRAP) offers early detection of sensitized workers and helps to more quickly address the problems of those experiencing asthma at work. The RRAP includes designated physicians from the public occupational health network, who have the support of lung specialists.

2.1.1 Absorption and metabolism

In the workplace, isocyanates are mainly absorbed through the respiratory tract. Caution must be exercised, since the odour threshold is much higher than the permissible exposure values.

> Odour can therefore not be relied on as a way of detecting the presence of isocyanates, and the way in which these substances are used has a major impact on potential exposure.

For example, the spraying of isocyanates during the application of coatings (paint) in aerosol phase disperses them into the air (causing inhalation if adequate preventive measures are not in place), while the application of a joint sealer using a caulking gun generates little or no airborne isocyanates but could lead to skin contact. Clinical trials using bronchial provocation tests have indicated that 60% to 91% of the hexamethylene diisocyanate (HDI) inhaled is absorbed by the lungs and rapidly hydrolyzed into amines. It thus makes its way into the blood, where it combines mainly with albumin (serum protein) and is distributed throughout the organism by the circulatory system. Dermal absorption is still the subject of controversy; the few studies available suggest a dermal absorption of less than 1% in 24 hours for diphenylmethane-4,4′ diisocyanate (MDI) and toluene diisocyanate (TDI). Some studies on rats suggest that this type of exposure could play a role in the triggering of pulmonary sensitization. Lastly, absorption through the digestive tract is improbable, but could occur in cases of poor hygiene.

2.1.2 Biomarkers

Biomarkers are substances found in the body following the absorption of a specific chemical substance. They can be good indicators of occupational exposure. In the case of isocyanates, polyamines are normally detectable following occupational exposure. The same is true of the protein adducts found in the blood. Controlled exposures to TDI and MDI have led to rapid detection of adducts and acetylated diamines in urine, the principal route of excretion of TDI and MDI. Animal research has also shown that a small quantity is found in the epithelial cells of the lungs and in the blood more than 18 hours after exposure. Biological monitoring has several limitations, including the half-life of diamines, which is several weeks for MDI in plasma, whereas elimination is much more rapid for TDI and HDI metabolites, namely toluene diamine (TDA) and hexamethylene diamine (HDA). Biomarkers could be a promising avenue for monitoring exposure, especially dermal exposure, if associated with a constantly measured exposure level.

> Biomarkers can confirm isocyanate exposure but cannot link it with the onset of disease. Moreover, the simultaneous presence of polyamines in the workplace would cause interference, since the two families of products give rise to the same biomarkers.

Isocyanates also act as haptens by attaching themselves by covalent bond to a circulating protein (albumin, laminin or cell membrane protein) to form an antigen and produce an immune reaction. This would lead to the formation of immune biomarkers (e.g., immunoglobulin E or G, IgE or IgG), which are commonly used biomarkers but have a weak correlation with the disease. Many workers presenting these immune biomarkers have not developed isocyanate-related asthma, while others who do have asthma do not have the biomarkers. Actually, the mechanism leading to allergy is not very well understood for isocyanates.

2.1.3 General toxicity

The reactive properties of isocyanates manifest simultaneously in three ways in the body. First, they are powerful irritants whose action will be felt on the skin and on all mucosa with which they come into contact (nose, eyes, throat). Next, once they are in the body, they can bind with proteins and trigger an allergic process. And finally, they have the ability to act directly – like medication – on the smooth muscles of the bronchi to make them contract. Isocyanates are therefore described as being at once irritative, immunological and pharmacological. Each of these properties will act in a variable way depending on the intensity and frequency of exposure, the susceptibility of the individual and the anatomical location of the isocyanate molecules. If all possible combinations are taken into account, the manifestations associated with isocyanates form a veritable continuum of pathologies, ranging from eye irritation to hypersensitivity pneumonitis and from contact dermatitis to asthma. Problems of pulmonary irritation will be dealt with first, since the most severe and frequent clinical manifestations observed in workers have to do with attacks on the respiratory system.

Acute effects

All isocyanates cause skin irritation (redness, dryness, eczema) that can reach the point of third-degree burns. Some studies also report allergic contact dermatitis. Exposure to vapours and aerosols causes eye irritation manifested by tearing, a burning sensation or even conjunctivitis, along with irritation of the upper respiratory tract causing throat pain or nasal drip. High airborne concentrations can cause ocular and nasal irritation. High-level exposure, for instance in the event of an accidental spill, can cause bronchial irritation that will manifest as reactive airways dysfunction syndrome (RADS), alveolar irritation (pneumonitis) and pulmonary oedema; the latter may occur up to 48 hours after exposure.

REACTIVE AIRWAY DYSFUNCTION SYNDROME (RADS)

Acute reactive airway dysfunction syndrome (RADS) is caused by very high exposure to isocyanates, usually more than 2 ppm, such as can occur during an accidental spill. In Québec, the eight-hour time-weighted average exposure value (TWAEVs) are 0.005 ppm for HDI, MDI and TDI monomers, isophorone diisocyanate and dicyclohexylmethane diisocyanate-4,4′, and 0.02 ppm for methyl isocyanate. Although isocyanate oligomers are not specifically regulated in Québec, they do contribute to toxicity, often in a major way since they are present in very high proportions in certain products. They account for more than 99% of the isocyanate functional groups in HDI-based paint mixtures, for example. The *Regulation respecting occupational health and safety* (ROHS) clearly states that exposure must be kept to a minimum for all isocyanates. RADS, which is actually a burn inflicted on the bronchial tract, is characterized by persistent cough, wheezing, shortness of breath and tightness in the chest. It affects all workers exposed to high isocyanate concentrations. Physical effort and cold are among the factors that can aggravate the symptoms. It is therefore critical for workers suffering from RADS to rest and see a doctor. The symptoms can take up to 24 hours to manifest, and the ensuing bronchial hyperreactivity lasts several months. In some individuals, a single exposure of this type is enough to sensitize them for life. In other words, they will present actual asthma symptoms each time they are in the presence of even very small quantities of isocyanates, i.e., at concentrations far lower than the permissible limits.

PNEUMONITIS

Pneumonitis is a consequence of inflammation caused by exposure of the pulmonary alveoli to isocyanates. Liquid then infiltrates the alveoli, and the worker presents flu-like symptoms: fatigue, shortness of breath, cough and fever, which last several hours. In the worst cases, actual pulmonary oedema and respiratory distress can be observed.

Chronic effects

Chronic effects can be of the irritative or allergic type. Allergies manifest in the form of asthma when the bronchi are affected, or in the form of allergic alveolitis when the alveoli are implicated. These lung diseases cannot always be clinically distinguished, and a combination of symptoms of both types of disease is often observed.

HYPERSENSITIVITY PNEUMONITIS (ALVEOLITIS)

Hypersensitivity alveolitis is an inflammatory reaction of the terminal bronchioles and the alveoli, triggered by an allergic mechanism following inhalation of isocyanates. It appears six to eight hours after two or more exposures, and presents as flu-like symptoms: fatigue, aching joints, fever, discomfort, coughing, shortness of breath, chills, muscular aches. Normally, the worker will recover after 24 to 48 hours of rest. If exposure continues, the workers may develop a chronic form leading to exertional dyspnoea, coughing with expectoration and weight loss. These situations are more common with MDI than with TDI.

ISOCYANATE ASTHMA

Asthma is a respiratory syndrome caused by an inflammatory reaction of the bronchi. Three separate mechanisms cause the bronchi to contract: oedema (swelling) of the bronchial lining, contraction of the bronchial muscles and secretion of mucus at the centre of the bronchi. The subject presents bronchial obstruction caused by inflammation, thickening of the bronchial walls and constriction of the bronchi by the smooth muscle surrounding them. This narrowing hinders air flow, especially during exhalation. The symptoms are irritation of the eyes, nose and throat, coughing and episodes of wheezing. They usually occur in the evening, or can wake the worker during the night (this is called delayed response). Over time, the worker feels the symptoms more and experiences discomfort both during and after work (immediate and delayed response). In Québec, some 25% of recognized occupational asthma cases are caused by isocyanates, while the older literature reported that 5% to 15% of all exposed workers developed isocyanate-related occupational asthma in the course of their working life. Nevertheless, the annual incidence has dropped to less than 1% since the 1980s, thanks to better workplace awareness of the potential risks and ways to control them, better control of the work environment, the formulation of certain commercial products (for example, coatings containing fewer volatile monomers) and the use of respiratory protection equipment (RPE) when control at source is not possible. These preventive measures have reduced the incidence of new cases of occupational asthma.

Asthma is above all an inflammatory phenomenon triggered by an allergic response, and isocyanates are irritative molecules that can directly cause such inflammation in the bronchi. Isocyanate-related occupational asthma has a latency period, that is, the worker may be exposed for months or even years before becoming sensitized and developing asthma. If the worker, having become allergic, is again exposed to the causative agent, the symptoms may manifest rapidly or later, even during the evening or night. This is why some asthmatic workers do not connect their symptoms (coughing, abundant secretion, wheezing and difficulty breathing) with workplace exposure. The fact that the symptoms lessen or disappear on the weekend or during vacations suggests that they are of occupational origin. Some sensitized subjects removed from any exposure will recover, partially or completely. But the prognosis for a sensitized worker who remains exposed to isocyanates is not good: aggravation of symptoms, asthma attacks following exposure to very low doses of the causative agent, and permanent lung damage. Some deaths have also been reported. Moreover, some workers who have developed isocyanate-related occupational asthma may experience symptoms following exposure to any other lung irritant. This is called exacerbated or aggravated asthma.

Principal risk factors

Several factors can contribute to the development of asthma. Atopy – a genetic predisposition to allergies (e.g., hay fever, dust allergy) – does not seem to contribute to the triggering of isocyanate-related asthma, any more than gender, smoking or pre-existing asthma. In many subjects, sensitization is related to short but intense exposure (peaks). The higher the isocyanate concentration, the greater the risk of sensitization.

Based on current knowledge, it is not possible to determine whether isocyanate sensitization is caused solely by very high exposure or whether repeated low-dose exposures over a long time can also lead to asthmatic sensitization. Continuous rather than intermittent exposure to the causative agent seems to increase the risk of developing occupational asthma. Once sensitized, the worker will react to very low concentrations, well below the permissible value.

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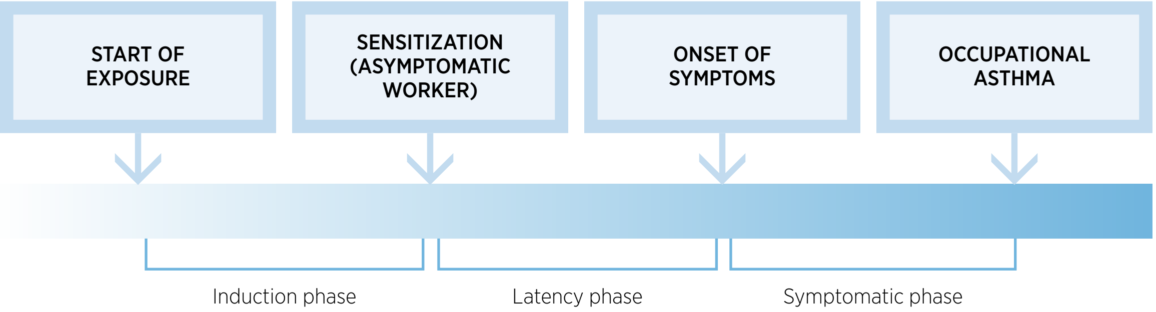
History of the disease

The natural history of the disease can be divided into three phases (Figure 2.1). The **induction phase** marks the beginning of occupational exposure and the start of early modifications, when the individual is completely asymptomatic. This is followed by the **latency period**, which separates the first biological modifications – reversible or irreversible, but asymptomatic (in this case, sensitization to the agent) – and the appearance of asthma symptoms. Early intervention during these first two phases will prevent damage before the disease can cause symptoms of occupational asthma. The **symptomatic phase**, where asthma symptomatology appears but the individual has not yet sought medical help, is the third phase. Early diagnosis can sometimes prevent more severe functional incapacities, which may already be present if the disease is diagnosed later.

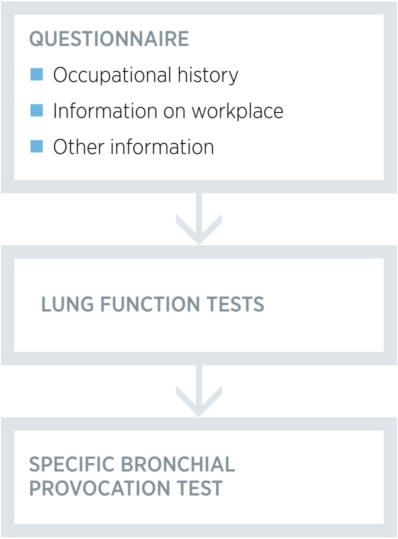
FIGURE 2.1

NATURAL HISTORY OF ASTHMA



Source: Adapted from: http://www.asthme.csst.qc.ca.

Diagnosis of occupational asthma



There are several ways of diagnosing occupational asthma. Questionnaires can be used not only for screening but also to document work history and obtain information about the workplace. Lung function tests provide a non-specific assessment of bronchial calibre, excitability and irritability. Specific bronchial provocation tests can also be conducted through controlled exposure of the patient to the causative agent (isocyanates) in a hospital laboratory and measurement of the patient's lung function.

Prognosis

Prognostic studies of occupational asthma have shown that a large proportion of sensitized workers still present respiratory symptoms many years after exposure to the causative agent has ceased. An estimated one quarter of subjects recover fully, once they are no longer exposed. **In other words, the great majority will suffer from bronchial hyperreactivity, which could contribute to sensitization to other commonplace allergens (aggravated asthma)**. A worker with occupational asthma has more chance of not suffering permanent consequences if the necessary measures are taken to control his or her exposure and to treat the disease as soon as possible after the onset of symptoms (third phase of the disease history). **An asthmatic worker should be reassigned to a job where there is no exposure to the causative agent**.

Once the disease is diagnosed, the worker must be removed from the workplace, since the risk of persistent asthma will increase if the worker remains exposed to the causative agent.

Mutagenicity and genotoxicity

It is not possible to determine, based on the available data, if isocyanates are mutagenic or genotoxic.

Reproduction and development

Studies on HDI, MDI, polymeric MDI (PMDI) and TDI do not show any teratogenic effects or any damage to the reproductive organs of exposed rats.

Epidemiologic and carcinogenicity studies

Rats and mice exposed to TDI by force-feeding showed an increased incidence of tumours similar to those found with TDA, a hydrolyzed derivative of TDI, especially in the subcutaneous tissue, pancreas, livers and mammary glands of rats and in the blood vessels and livers of mice. Inhalation did not lead to detection of any tumours in the animals. In February 1998, the International Agency for Research on Cancer (IARC) classified TDI as a probable carcinogen for humans (group 2B), while MDI and HDI are currently not considered carcinogenic.

Epidemiological studies on more than 4,000 workers in Sweden (1993 and 2004), more than 4,600 in the U.S. (1996) and more than 8,200 in the United Kingdom (1993 and 2003) failed to establish any causal link between isocyanates and cancer. The American Conference of Governmental Industrial Hygienists (ACGIH®) does not classify any isocyanate as carcinogenic for humans. That organization is considering the possibility of classifying TDI as a confirmed carcinogen for animals (*A3, Notice of Intended Changes*, ACGIH® Booklet 2012), while the National Toxicology Program (NTP) lists TDI as a substance reasonably anticipated to be a carcinogen on the basis of animal studies. The International Programme on Chemical Safety (IPCS) and the European Commission (EC) consider TDI to be a possible human carcinogen.

Health surveillance

Workers exposed to isocyanates should undergo regular medical examinations, especially for their lungs. This is a secondary preventive measure designed to detect early signs of sensitization before the onset of any disease, including occupational asthma. The surveillance program consists of a questionnaire on the person's occupational history and symptoms; depending on the result, medical consultations and lung function tests may be recommended (see History of the disease). The program has its benefits not only in the information gathered but also in worker awareness and occupational hygiene measures. Health surveillance should lead to detection of cases in their early stages, before the disease has fully developed. A medical examination should also precede the return to work of any worker who suffers cardiac or respiratory disease. In addition, there should be a medical follow-up after any accidental exposure and whenever any respiratory symptoms are manifested.

Québec has set up the Réseau de référence pour l'asthme professionnel (RRAP) to accelerate the management and treatment of workers experiencing occupational asthma. RRAP is a network of designated physicians in the public occupational health system who are supported by lung specialists. It is a referral network; workers come to it of their own volition. The process begins when a worker is provided with information by the OHS (Occupational Health & Safety) team, along with a questionnaire to be filled out on a voluntary basis. Workers who present symptoms are encouraged to contact the company nurse or physician in order to begin the process.

In sum, isocyanates are powerful skin and respiratory irritants and sensitizers, capable of causing occupational asthma. In the absence of strong exposure peaks, current literature suggests that an average exposure of less than 0.005 ppm and peaks of less than 0.020 ppm in **total isocyanate functional groups** (ppm of NCO groups) lead to an annual occupational asthma incidence of less than 1% in non-sensitized workers. Health surveillance is important in diagnosing asthma as soon as possible to minimize the potential for permanent damage.

Controlling occupational exposure is still the best way of fighting the development of isocyanate-related occupational diseases.

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2.2 LEGISLATION

Today's legislation has as its aim the reduction and even elimination of the risks posed by the use of hazardous substances, including isocyanates.

In this section we will examine the laws and regulations related to isocyanates in order to determine each party's responsibilities and obligations regarding the control of isocyanate use.

2.2.1 Employer's responsibilities

The Workplace Hazardous Materials Information System (WHMIS) is governed by federal and provincial laws and regulations. Employers in Québec are subject to provincial legislation, in particular the Act respecting *Occupational Health and Safety* (AOHS) and the *Regulation respecting information on controlled products*.

The use, handling and storage of a controlled product in a workplace are authorized if the container bears a label and the manufacturer supplies an MSDS complying with the provisions of the Act (AOHS, sections 62.1 to 62.4, 62.6) and its regulations. Moreover, workers must have received the training and information required to safely perform the task assigned to them (AOHS, Section 62.5).

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is an international system for labelling of materials that are hazardous to human health or the environment. Its purpose is to unify the different national systems, including WHMIS and the hazardous goods transportation regulation. Several new hazard pictograms (link in French only) are to be established. One showing a white mass inside a human bust (Figure 2.2[2]) has been introduced and is used to identify respiratory sensitizers. At the time of publication, the GHS had not yet been implemented in Québec.

FIGURE 2.2

GHS PICTOGRAM

The employer must take the necessary steps to protect workers' health and ensure their safety and physical well-being as stipulated in the AOHS, Section 51, which further states the employer's obligations with regard to:

1. equipment and workplace layout and maintenance;
2. work organization, methods and techniques;
3. identification, control and elimination of risks, including risk of fire and of exposure to contaminants;
4. providing workers with training and information, in particular on personal protective equipment (PPE);
5. requiring workers to wear PPE.

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[2] Online source of health hazard pictogram used for identification of respiratory sensitizers: http://www.ctconstruction.org/files/public/Pictogram-summary.pdf (April 2013).

2.2.2 Ventilation

Isocyanates are contained in many products such as vehicle coatings and primers, polyurethane foam and binders (see Anticipation). They constitute a hazard to worker health and safety and can induce occupational asthma (OA) as well as skin allergies (see Effects on health).

Ventilation must reduce or even eliminate isocyanate exposure through preventive measures, a number of which are prescribed in sections 101 to 104, 107 and 109 of the *Regulation respecting occupational health and safety* (ROHS).

The ROHS also states that air intakes must not introduce contaminated air (Section 106), and that contaminated air must be discharged without being recirculated (Section 108) or released into adjacent facilities (Section 110).

Sections 27 to 40 of the Clean Air Regulation (chapter Q-2, r. 4.1) prescribe atmospheric emissions standards for the application of paints and coatings. These standards are especially concerned with the emission of volatile organic compounds (VOCs) resulting from the presence of organic solvents in paints: they specify emission thresholds, maximum paint VOC content and paint application equipment requirements. Since the isocyanates in paint are not solvents but binding agents, they are not covered by the CAR emissions standards.

2.2.3 Air quality

Under Section 39 of the ROHS, all dangerous substances that are sources of dusts, fumes, mists, vapours or gases must be eliminated or at least reduced through replacement with other products. If replacement is not feasible, the concentrations of these dangerous substances in a worker's breathing zone must not exceed the permissible exposure values (PEVs) listed in ROHS Schedule I (Section 41).

For an establishment with more than 50 workers, the ROHS specifies that contaminant concentrations must be measured at least once a year if they exceed or are liable to exceed the PEVs listed in ROHS Schedule I. Measurements must also be taken each time an industrial process is modified or controls are installed. The results of air quality measurements must be kept for at least five years (ROHS, Section 43). The measurements must be taken in the worker's breathing zone if possible, using the methods described in the sampling guide published by the Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST) (ROHS, Section 44).

In addition, Section 42 contains specific requirements regarding exposure to diisocyanates and isocyanate oligomers; such exposure must be kept to a minimum, even when it remains within the PEVs listed in ROHS Schedule I.

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> The concept of minimal exposure (EM in the ROHS) can be interpreted as follows:
>
> A study is conducted of the level of risk associated with the process and the substance (volatility, physical form), the objective being to identify prevention measures that could be adapted to the specific situation. This is done on a case-by-case basis. The hierarchy of prevention measures is studied: substitution, isolation of the process, ventilation, etc. and, as a last resort, the use of cartridge respirators if the exposure is of short duration and no aerosol is emitted. If aerosols are emitted, supplied-air respirators are the preferred means of protection.

Although exposure control must be a function of the exposure level, and although the anticipation and recognition stages refer to information on the chemical nature of the isocyanates present, their health effects, regulations in effect, etc., risk quantification is not included in the risk level study proposed in the approach described in the box above. The concept of minimal exposure (notation EM in the ROHS) supports this approach and the preventive measures.

Reference values

To prevent harmful health effects and occupational diseases that can result from worker exposure to chemical contaminants, it is important to recognize and evaluate the exposure so that preventive measures can be implemented (ROHS, sections 43 and 44). The evaluation strategy is based principally on measuring exposure and comparing this concentration against reference values (RVs).[3]

Environmental sampling targets the exposure sources by concentrating on high-risk tasks. In addition, although the intensity, duration and frequency of the exposure linked to the onset of disease are not always known, new isocyanate exposure values could be based on short-term excursions rather than on the weighted eight-hour average. It is easier to determine exposure peaks, which can contribute to the development or exacerbation of disease, by referring to short-term exposure values. The S notation in ROHS Schedule I classes isocyanates among respiratory sensitizers.

Some organizations or countries, such as Australia, the United Kingdom and Switzerland, have established reference values corresponding to a concentration expressed as the weight of all isocyanate functional groups together per unit of air volume, i.e., µg of NCO per cubic metre (m^3), including the isocyanate groups of monomers AND oligomers. This quantification parameter is insensitive to the rapid development of new isocyanate-based product formulas (see Sampling and analysis). Given that monomers are much less present than oligomers in many of the mixtures used, establishing a reference value for oligomers (polyisocyanates) is the only way to ensure a quantitative evaluation of the real overall risk of exposure and thus to take adequate measures to protect workers, considering their sensitizing effect. The tables in Appendix 1 show the reference values for five substances in the isocyanate family. The designations used in these tables as well as the footnotes to the tables have been harmonized to facilitate consultation. The values are taken from the hazardous substances database (GESTIS).

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[3] Depending on the organization or country, reference values can also be called threshold limit values, exposure limits, permissible exposure limits, maximum exposure limits, workplace exposure limits (TLV, EL, PEL, MEL, WEL) etc. Generally speaking, they are an eight-hour time-weighted average (TWA), a 15-minute exposure limit (short term exposure limit, or STEL) or a ceiling. A sample list of exposure limits is presented in Appendix 1.

2.2.4 Personal protective equipment

Employers must provide free personal protective equipment (PPE) to their workers. The section Controlling risk factors lists the materials to be used in gloves and coveralls to ensure protection against isocyanates.

! The wearing of PPE in no way eliminates the employer's obligation to reduce at source the hazards to worker health and safety (ROHS, Section 45).

The Occupational Safety and Health Administration (OSHA) warns that there are no cartridge respirators equipped with end-of-service indicators approved for isocyanates by the National Institute for Occupational Safety and Health (NIOSH). However, OSHA considers that, where it is impossible to use supplied-air respirators, the use of activated-charcoal cartridges may be acceptable if there is an effective and controlled program for cartridge change in the absence of an end-of-service indicator.

The establishment must have a respiratory protection program (ROHS, Section 45) that includes worker training and respirator adjustment and tightness tests. The choice of respirator and its protection factor (PF) must also be documented in this program.

2.2.5 Deflagration hazard

Isocyanate-based products also contain inflammable solvents. In addition to the chemical risk inherent in these substances, the risk of deflagration and fire must therefore be taken into account in the design and layout of workplaces where they will be used, especially paint shops and booths. Such areas and equipment must meet the specifications of the Québec Construction Code and must observe safety principles. The ROHS states that it is necessary to:

1. eliminate sources of inflammation, including static electricity (ROHS, sections 50 to 52);
2. keep concentrations of inflammable vapours under 25% of the lower explosion limit (ROHS, Section 49);
3. adequately design systems for local exhaust of inflammable vapours or gases (ROHS, Section 53);
4. ensure optimum operation of exhaust systems during operating hours (ROHS, Section 5).

The system for collecting and processing spray and other contaminants presenting a fire and explosion hazard must be designed, built, installed, used and maintained according to industry good practice and the standards prescribed in Section 58 of the ROHS.

More information on this topic can be found in the National Fire Protection Association's Flammable and Combustible Liquids Code (NFPA-30, 2012), the standard on Spray Application Using Flammable or Combustible Materials (NFPA-33, 2011) and the National Fire Code of Canada.

Inflammable substances must be stored in accordance with WHMIS specifications and with ROHS Sections 81 and 82.

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ENVIRONMENTAL EVALUATION

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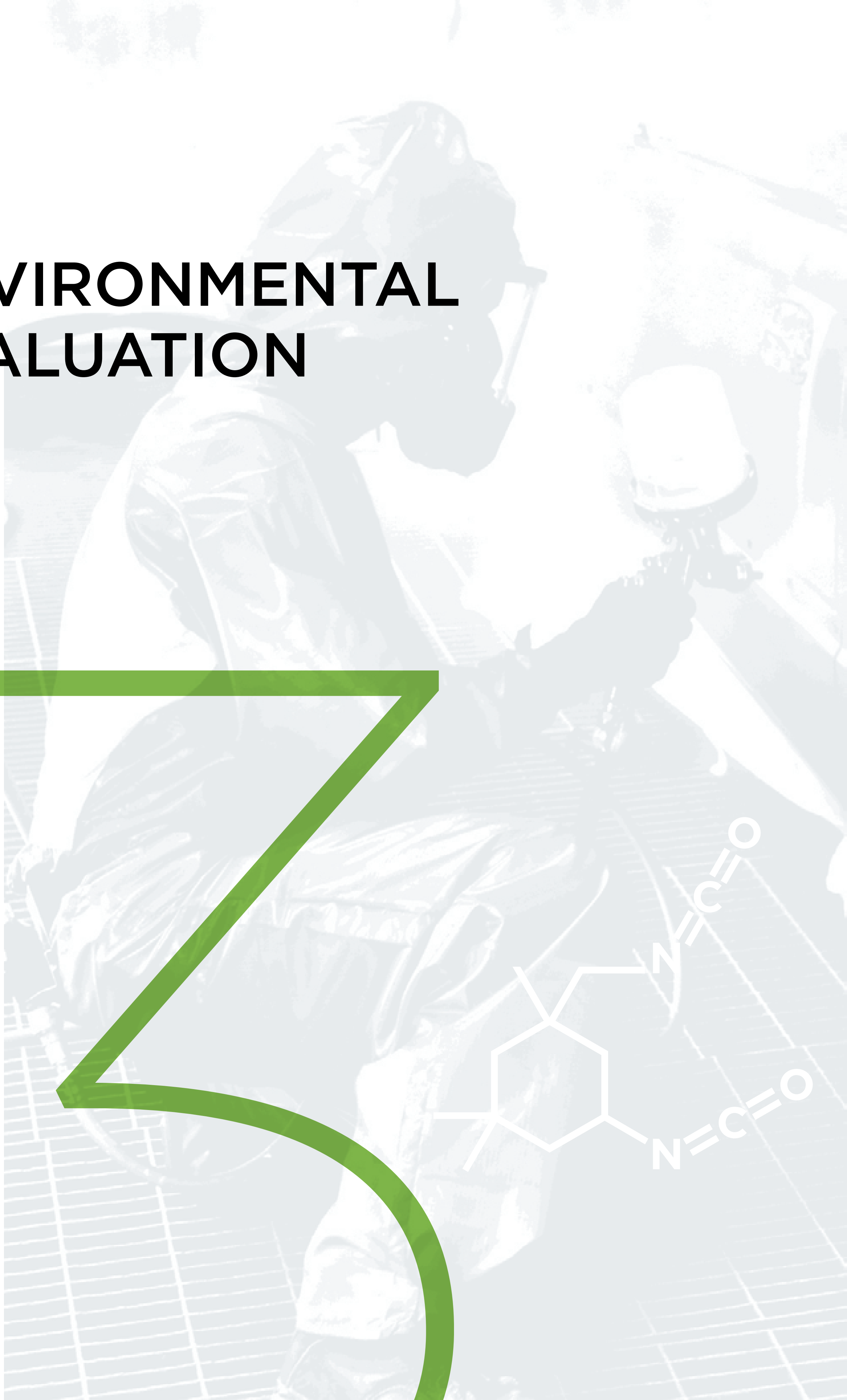

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ENVIRONMENTAL EVALUATION

Worker exposure is a function not only of the characteristics of the isocyanate present, but also of its use, the process and the equipment. In certain processes, isocyanates are generated in different physical forms (vapour, aerosol) and chemical forms (monomer, oligomer), each with its own potential health hazards.

In evaluating the health risks of a substance, exposure factors and determinants must be taken into account: for example, the toxicity of the substance in question, its properties and physical form, environmental conditions (temperature and humidity), the processes used (see Anticipation and Sampling and analysis), the routes of absorption (see Effects on health) and the work schedule. The environmental evaluation supports the implementation of control measures (substitution, ventilation, PPE, etc.).

Considering the potential of isocyanates to cause skin irritation and obstructive pulmonary diseases including OA, the exposure assessment must make it possible to determine isocyanate concentration (1) in the air, in the form of vapour or aerosol and (2) on work surfaces, depending on the reactivity of the monomer and oligomer forms. For instance, an isocyanate-based coating applied with a roller or brush might emit vapours, whereas it might emit aerosols as well if sprayed on. The objective of an intervention (Figure 3.1) could be to assess worker exposure as part of the development of a prevention program, a compliance study or an air quality study for reintegration of a sensitized worker. Attention must also be paid to work surface contamination, which can contribute to dermal exposure. Biological monitoring can confirm exposure through these two main channels, i.e., inhalation and skin contact, if the isocyanate polyamines in question are detectable.

FIGURE 3.1

ISOCYANATE EXPOSURE ASSESSMENT

Whether for a compliance study or other purpose, the result of an exposure assessment is compared against the reference values (eight-hour time-weighted average exposure value [TWAEV] or 15-minute exposure value [STEV]). The air sampling and analysis methods must characterize the isocyanates in the physical forms (vapour and/or aerosol) and chemical forms (monomer and oligomers) generated by the process (see Sampling and analysis). The periods[4] when samples are not taken must be thoroughly documented in order to estimate the exposure potential they represent. Inhalation and dermal exposures for several processes are described in detail in sections 3.1 and 3.2 respectively.

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[4] For more information, see the IRSST's *Sampling Guide for Air Contaminants in the Workplace*.

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ENVIRONMENTAL EVALUATION

During a study for relocation of a sensitized worker, it is important to ensure that the ambient air at the workstation is free of isocyanates. The choice of analytical method is crucial in terms of the levels to be quantified, which are probably very low; a high-sensitivity method must therefore be used (see Sampling and analysis).

3.1 INHALATION EXPOSURE

As mentioned in the section on Anticipation, many industrial processes use monomeric or oligomeric isocyanates. Spraying poses more of a hazard for workers than injection, extrusion or other processes.

3.1.1 Exposure during spray application of vehicle coatings

The isocyanates contained in primers, hardeners, topcoats and other products are monomeric HDI and a variety of combinations of four polyisocyanates: isophorone diisocyanate (IPDI) polyisocyanate, biuret HDI, uretidione HDI and isocyanurate HDI. Studies show that workers in auto body shops are frequently exposed to high levels of oligomeric HDI. The main factors at play in the automotive repair industry are as follows:

1. Quantity of coatings used
2. Shop characteristics
3. Number of vehicles to be painted
4. Number of painters present
5. Speed and type of draft in the finishing booth (downdraft, semi-downdraft and crossdraft)
6. Work practices
7. Environmental conditions

The literature reports that exposure is less in a large shop where many topcoats are applied. This is due to the greater air volume in this type of shop, along with more modern equipment and preventive maintenance programs. The potential for exposure of workers not involved in spray coating operations is reported to be higher in small shops, especially during cold weather when the doors, windows and other openings are kept closed. Concentrations reported in the literature are shown in The industrial hygiene approach – Examples.

3.1.2 Exposure during spray application of urethane foam

Spraying of diphenylmethane-4,4′ diisocyanate (MDI) based rigid foam is used in building insulation. MDI is mainly present as an aerosol of fine particles (mostly > 10 µm). The aerosol phase of the liquid greatly increases the liquid/air surface, one of the factors in evaporation. In aerosol phase, a liquid will pass more easily into the vapour phase (up to the saturated pressure). The literature reports that the installer is subjected to a high level of exposure, with monomeric MDI concentrations ranging from 11 µg/m^3 to 1800 µg/m^3. Although the levels are lower for assistants, they depend mainly on the work practices employed. Finally, exposure increases when spraying takes place in closed or small spaces. In Québec, the TWAEV for MDI is 51 µg/m^3 (see Table 3 in Appendix 1).

An MDI-based foam is injected to consolidate underground tunnels. During this process, the reported MDI concentrations range from the limit of quantification up to 300 µg/m^3 of NCO (active isocyanate functional groups).

MDI is also used in the manufacture of vehicle interior accessories (extrusion) and their binding agents. Workers assigned to the manufacture or gluing of these accessories may be exposed to concentrations of 115 µg/m^3 to 352 µg/m^3. The concentrations reported in the literature are shown in The industrial hygiene approach – Examples.

3.1.3 Exposure during use of isocyanates as binders

For the past few years, MDI has been used in the manufacture of oriented strand boards, or OSB. Eight-hour TWA at workstations evaluated is reported to range from the method quantitation limit to 524 µg/m^3. According to the literature, the exposure groups are not always homogeneous; the operator assigned to cleaning of the dryers and mixer has a higher exposure risk than other workers.

The use of isocyanate-based binders can generate isocyanate vapours if a heated caulking gun is used. As the temperature rises, so does the vapour pressure; hence the increased presence of isocyanates in the vapour phase.

Workers assigned to gluing may be exposed to MDI concentrations ranging from 12 µg/m^3 to 47 µg/m^3. Foam manufacture by moulding or high- or low-pressure extrusion also presents an isocyanate exposure potential (TDI or MDI). The concentrations reported in the literature are shown in The industrial hygiene approach – Examples.

3.1.4 Exposure during thermal degradation

Thermal degradation of polyurethane causes the release of isocyanates and other toxic substances such as aminoisocyanates and amines in the form of vapours and very fine particles (< 2 µm). The isocyanates are mainly monomeric.

The use of an abrasive process (disk grinding, finishing sanding, cutting, etc.) on isocyanate-based coatings generates heat that can cause isocyanates – including MDI, HDI, TDI, IPDI and methyl isocyanate (MIC) – to become airborne. The exposure potential is greater during cutting operations. Given that this task can generate isocyanate concentrations of up to half the exposure limit recommended by the Health and Safety Executive (HSE), it should not be done by a sensitized worker. Welding and machining of metals with polyurethane-based coatings can generate airborne isocyanates, including MIC, HDI, IPDI, TDI and MDI, along with their corresponding amines, depending on the type of coating applied.

In foundries using hot box core binders, MIC exposure is low in comparison with the threshold limit values recommended by the American Conference of Governmental Industrial Hygienists (ACGIH®). A medical exam, adequate ventilation and preventive measures related to production methods are recommended.

Newly formed flexible foam discharges TDI when cut with a hot wire. However, no TDI is detected during cutting of a foam more than 24 hours old. The concentrations reported in the literature are shown in The industrial hygiene approach – Examples.

Regarding the risks linked to situations such as a burning vehicle for example, linear aliphatic isocyanates, alcenic isocyanates (from methyl to butyl) and HDI are generated mainly during the combustion of the vehicle coating.

3.2 EXPOSURE BY SKIN CONTACT

Isocyanates can be absorbed through the skin, usually when a contaminated surface is touched or when material is projected. In addition to being exposed through inhalation, auto-body workers are exposed cutaneously, especially to HDI, during coating preparation (if adequate gloves are not worn), spray application and work on a coating that is not yet completely dry. The average drying time is about 56 hours; thus there is the potential for dermal exposure during that time.

In OSB manufacture, MDI contamination of surfaces has been observed at workstations where there is an accumulation of wood dust and/or MDI residues.

In some circumstances, it can be useful or even necessary to determine the presence, nature or approximate quantity of isocyanates on table tops, tools or other objects.

> Wipe-sampling poses a particular challenge because these highly reactive substances contain several isocyanate functional groups, some of which may be chemically bonded to the surface on which they are found and therefore difficult or impossible to sample (see Methods for assessing isocyanates on surfaces).

3.3 SAMPLING AND ANALYSIS

Isocyanates are highly reactive molecules. For adequate laboratory analysis, they must be "converted" into more stable molecules *in situ* immediately after sampling. The efficacy of the "conversion" is directly linked to the characteristics of the isocyanates present in the workplace, which will have a determining influence on the type of sampler to use. The choice of exposure assessment method will therefore depend on all of these characteristics, which are linked to the isocyanate type and the process.

In this section we will review the various methods for obtaining the best possible exposure data. Case studies are presented in The industrial hygiene approach – Examples. Note that the sampling and analysis strategies cited in this document are those recommended by the IRSST, although there are others.

3.3.1 General principles

Because isocyanates are highly reactive molecules, the method used to assess exposure will almost always be a variation on the following sampling and analysis principle:

> The isocyanate is captured on a substrate and immediately (or within a very short time) placed in contact with a chemical reactant, which will convert the isocyanate into a more stable molecule that will be easier to analyze.

TABLE 3.1

ISOCYANATE CHARACTERISTICS TO TAKE INTO ACCOUNT IN SAMPLING AND ANALYSIS

CHARACTERISTIC	DESCRIPTION – DETERMINANT
Chemical form	Monomer and/or oligomers, in relation with: ■ process
Physical form	Vapour or aerosol, in relation with: ■ chemical form (vapour pressure) ■ process (temperature, mechanical dispersion)
Reaction speed	Slow or rapid, in relation with: ■ chemical form ■ process

This statement indicates that exposure measurement generally consists of two steps: **sampling** and **analysis**. These two steps are inextricably linked, and the quality of the result is dependent on each one to an equal extent. The sampling can be done in the air or on a surface, while the analysis can take place either *in situ* or in the laboratory. The ability of these two steps to provide the user with accurate data on isocyanate exposure for a given workplace, task or process is a direct function of their adaptability to the properties and characteristics of the isocyanates and process used. To facilitate a better understanding of the impact of these aspects on exposure assessment, Table 3.1 and the subsequent paragraphs review the information presented under the heading Anticipation. The table summarizes the isocyanate characteristics that must be known before one can proceed with an assessment of inhalation exposure. It can be seen that the characteristics to be taken into account in exposure assessment are interrelated.

The **chemical form** of the isocyanates – monomeric and/or oligomeric – depends on what is needed for the process. For example, HDI-based paint contains less than 1% monomer and more than 75% oligomers, whereas in the production of flexible polyurethane foam, 100% of the TDI is in monomer form. As mentioned in the subsection Effects on health, all isocyanate functional groups, monomeric or oligomeric, are harmful to worker health. In addition, although a specific PEV is not mentioned as in the case of monomers, the ROHS designates oligomers as sensitizing (S) and stipulates that exposure must be kept to a minimum, which means their assessment in the workplace is mandatory when their presence is anticipated. To illustrate this, let us return to the case of HDI used in spray application coatings, where the concentration of airborne monomers may be well below the chosen action level while the oligomer concentration may be considerable and would thus become the sole indication of significant exposure to isocyanates.

The presence of isocyanates in the **physical form of vapour** depends on the vapour pressure of the chemical compound, an intrinsic property of its molecular structure. For example, the vapour pressure of monomeric HDI is greater than that of oligomeric HDI or monomeric MDI (see Table 1.1). However, the temperature of a process may lead to significant emissions of vapour-phase monomeric MDI. The presence of isocyanates in the **physical form of aerosols** depends on the process, i.e., whether it involves mechanical diffusion (spraying), physical attrition (sanding) or vapour condensation (welding, high temperature), and this in turn determines particle size – an important factor as it can affect the efficacy of a sampler. The particles formed during a spraying or sanding process are generally larger (aerodynamic diameter, AD > 10 µm) than those formed during vapour condensation (AD < 2 µm). The physical form or forms anticipated will dictate the sampling method to use. Generally speaking, aerosols of all sizes are collected on a filter, while an impinger can effectively collect vapours and aerosols with an AD of more than 2 µm. Coated filters are effective in the case of vapours.

The reactivity of isocyanates is one of their inherent characteristics, and is both sought after (for use in manufacturing processes) and a cause of apprehension (for its effects on health). Processes using isocyanates have different **reaction speeds**, and this difference will have a direct effect on the time allowed between the collection of the isocyanate and its conversion into a more stable chemical compound for laboratory analysis. For example, in a spraying process in which the aerosol is in the form of droplets containing the two components, i.e., the isocyanate-based product and the copolymer, the reaction could be so rapid that a sampler that does not stabilize the isocyanate *in situ* will cause an underestimation of the concentration. One sampler capable of stabilizing the isocyanate *in situ*, whether in vapour or aerosol form, is the impinger. A coated filter will not be very effective for large reactive particles, since the isocyanates' contact surface with the reagent will be relatively small.

It must be kept in mind that once the isocyanate has been totally polymerized in the final product (coating, insulating foam, binder, etc.), it cannot be analyzed. The challenge of evaluating these substances therefore lies in stabilizing the highly reactive isocyanate chemical group (NCO) so it can be analyzed in the laboratory. The OHS professional or technician must take these characteristics into account when choosing a sampling and analysis method.

3.3.2 Methods for assessing airborne isocyanates

Process sampling

If the OHS professional or technician does not have all the information needed to anticipate and recognize the isocyanates present in the workplace, a process sample (raw material, hardener, primer, etc.) may be sent to the IRSST laboratory for qualitative analysis.

IRSST Method 376 – Use of double-filter cassette in isocyanate determination

SAMPLING: Air is pumped through a closed-face 37-mm cassette with two filters. The first, a teflon filter, captures aerosols, while the second, a glass fibre filter (GFF) treated with the reagent MAMA (9-(N-methylaminomethyl) anthracene), captures vapour-phase isocyanates. After sampling, the teflon filter is removed from the cassette and placed in a jar containing MOPIP (1-(2-methoxyphenyl) piperazine) in toluene.

ANALYSIS: The two filters are analyzed separately by high-performance liquid chromatography with ultraviolet detection (HPLC-UV). Both monomers and oligomers are analyzed.

This method, developed at the IRSST in the late 1980s, uses a closed-face 37-mm cassette, which has been used in sampling techniques for decades (Figure 3.2). The device samples isocyanate vapours and aerosols in breathing zones and at specific workstations. In the presence of aerosols, sampling time is limited to 15 minutes (intake flow 1 L/min) due to the absence of reagent on the first filter. A longer sampling time is one of the causes of potential underestimation of isocyanates in the form of fast-reacting aerosols.

If only isocyanate vapours are anticipated, the sampling time may be extended up to eight hours, in which case a teflon filter analysis (aerosol isocyanates) will be useless. Hence the importance of adequately anticipating the presence of isocyanates solely in the vapour phase in order to avoid underestimating the total concentration.

Each sample produces two results: monomer concentration and oligomer concentration, each expressed in milligrams per cubic metre (mg/m^3). The monomer result comes from the sum of the quantity of monomer found on the teflon filter (aerosol fraction) and the glass fibre filter (vapour fraction). The oligomer concentration is obtained by analysis of the teflon filter.

> The oligomer result is calculated by combining the concentration obtained for each of the oligomers identified by the detector and quantified in reference to the detector response to the corresponding monomer. The oligomer concentration is thus expressed in the analysis reports as mg/m^3 monomer equivalent.

This method has been published as standard test methods by the American Society for Testing and Materials (ASTM International, D5932, D6561 and D6562) and the International Organization for Standardization (ISO 17736). Technical details and other information are shown in Table 3.2.

FIGURE 3.2

DOUBLE-FILTER SAMPLING CASSETTE FOR METHOD IRSST 376 (ISO-CHEK®)

Credit: Christian Sirard, IRSST

Credit: Dominique Desjardins, IRSST

Modified Method IRSST 376 – Use of impinger in isocyanate determination

SAMPLING: Air is pumped through an impinger containing MOPIP in toluene; the impinger may also be equipped with a cassette containing a MOPIP-coated glass fibre filter below the impinger.

ANALYSIS: In the laboratory, the solution from the impinger (and from the filter, if applicable) is analyzed by high-performance liquid chromatography with ultraviolet detection (HPLC-UV). Both monomers and oligomers are analyzed.

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This method is based on MDHS 25/3 of the U.K. Health and Safety Laboratory (HSL) – also an ISO standard test method (ISO 16702) – and uses an impinger (Figure 3.3) containing the reagent MOPIP in toluene to capture isocyanates in vapour and aerosol form at a fixed sampling station. The presence of a volatile solvent in a glass container is **not desirable for personal sampling in the breathing zone**. The main advantage of this method is that stabilization of the captured isocyanates is very effective, which is important when very fast-reacting isocyanates are to be assessed. If particles of less than 2 μm are anticipated, a cassette with a glass fibre filter coated with MOPIP is added below the impinger, since the impinger's collection mechanism is not effective for very fine particles. The sampling time has a limit that is not related to stabilization of the isocyanates collected on the substrate, but rather to evaporation of the solvent (toluene) in the impinger. Solution may, however, be added as needed during the sampling. To avoid underestimation, the cassette filter (if used) must be transferred to a jar containing MOPIP immediately after sampling.

A cautionary note applies to the pump used to take samples with an impinger. It is very important to have the pump validated by the IRSST, since it has been shown that the mechanism on certain pump models disintegrates in the presence of toluene vapour.

Each sample produces two results: the monomer concentration and the oligomer concentration, expressed in milligrams per cubic metre (mg/m^3). Both concentrations are obtained from the same impinger solution extract.

The oligomer result is calculated by combining the concentration obtained for each oligomer that the detector identified and quantified in reference to the response in the corresponding monomer detector. The oligomer concentration is thus expressed as mg/m^3 monomer equivalent in the analysis report. If a cassette was used, the quantity of isocyanates measured is combined with the monomer and oligomer results, as the case may be.

Technical details and other information on this method are presented in Table 3.2.

FIGURE 3.3

SAMPLING SETUP FOR IRSST METHOD 376 – IMPINGER

Sampling impinger

The sampling impinger may be kept in a pouch.

Cassette with MOPIP-coated GF filter (optional)

Trap

Photo: Dominique Desjardins, IRSST

IRSST method 366 - High-sensitivity determination of isocyanates

SAMPLING: Air is pumped through a closed-face 37-mm cassette that has two glass fibre filters coated with the reagent MAMA; vapour-phase isocyanates are captured in the filters.

ANALYSIS: In the laboratory, each filter is analyzed separately by high-performance liquid chromatography coupled with mass spectrometry (HPLC-MS).

Only the monomer is analyzed.

This method, which also uses a closed-face 37-mm cassette (Figure 3.4), is designed to measure very low concentrations of vapour-phase monomeric isocyanate. The device can be positioned either in a worker's breathing zone or at a fixed station, and the sampling time can be up to eight hours. This method is recommended for evaluating a work environment – in particular for the purpose of relocating a sensitized worker – to ensure that vapours are not propagating to areas where isocyanates are not used, such as offices. As mentioned in the section Effects on health, a sensitized worker could be severely harmed if exposed to isocyanates, even at concentrations well below the threshold value; hence the importance of using a method with a very low limit of quantification. Note that because of its very low limit of quantification, **this method should not be used** when a workstation uses isocyanates whose results are to be compared against a reference value, even if the type of emissions allows for this, i.e., when isocyanates in monomer form and vapour phase only are anticipated.

FIGURE 3.4

SAMPLING CASSETTE FOR IRSST METHOD 366 – HIGH SENSITIVITY

Credit: Christian Sirard, IRSST

Credit: Dominique Desjardins, IRSST

Each sample produces one result, usually expressed in nanograms per cubic metre (ng/m^3). Analyzing the two filters separately will show whether the first filter is saturated.

Technical details and other information on the isocyanate assessment methods offered by the IRSST are presented in Table 3.2.

TABLE 3.2

COMPARATIVE SUMMARY OF METHODS FOR ASSESSING AIRBORNE ISOCYANATES

	IRSST 376 DUAL FILTER	IRSST 376 IMPINGER	IRSST 366 HIGH SENSITIVITY
Isocyanates	HDI, IPDI, TDI and MDI	HDI, IPDI, TDI and MDI	HDI, IPDI, TDI and MDI
Sampler	37-mm cassette, teflon filter and coated GF filter	Impinger, 37-mm cassette (optional)	37-mm cassette, 2 coated GF filters
IRSST material code	917	1415	970
Shelf life	3 months	3 months	3 months
Oligomers	Yes	Yes	No
Vapours	Yes	Yes	Yes
Aerosols	Yes	Yes (if < 2 µm, add cassette)	No
Flow (L/min) **Max. volume (L)**	1.0 15*	1.0 –	1.0 –
Desorption *in situ*	Yes	No (except if cassette used)	No
Preservation of samples	4 weeks at 4°C away from light	4 weeks at 4°C away from light	4 weeks at 4°C away from light
Laboratory instrumentation	HPLC-UV	HPLC-UV	HPLC-MS
Minimum reported value MRV (µg/sample)	0.014-0.041 (varies according to isocyanate)	0.025-0.041 (varies according to isocyanate)	0.00075 (varies according to isocyanate)

* Depending on the context, the volume may be increased (sampling time > 15 min); see IRSST Method 376 – Use of double-filter cassette in isocyanate determination.

Expression of analysis results from IRSST Method 376

The analysis report produced by the laboratory contains the results, expressed in mg/m^3, and their minimum reported value (MRV), expressed in µg. Note that only the result reported for total monomers (sum of monomeric isocyanates in vapour and aerosol phase, when the double-filter cassette is used) may be used in calculations for determining the exposure level, which will then be compared against the corresponding RV. The result reported for oligomers rounds out the exposure assessment and makes it possible to take into account all the health effects of isocyanates and their EM designation in Section 42 of the ROHS (exposure to be kept to a minimum).

3.3.3 Methods for assessing isocyanates on surfaces

SAMPLING: A developer solution is applied on the surface. After 30 seconds, the surface is wiped with a pad treated with an indicator. If isocyanates are present, the pad will turn reddish-orange after a few minutes.

This type of qualitative method indicates the presence or absence of isocyanates on a surface. It is not necessary to know the quantity or concentration, since their presence alone indicates that the surface must be cleaned to eliminate the risk of dermal exposure. The developer solution/pad kit that the IRSST provides to its clients is a commercial product marketed under the brand name SWYPE™ (Figure 3.5). SWYPEs are available for aliphatic isocyanates (IRSST material code 3050) and for aromatic isocyanates (IRSST material code 3060).

FIGURE 3.5

SURFACE SAMPLING KIT

Photo: Dominique Desjardins, IRSST

A quantitative method developed by the OSHA in 2002 is also based on the use of wipes, but it requires subsequent laboratory analysis to obtain an isocyanate weight per unit of surface sampled. The IRSST does not offer this method, because of its potential limitations: there is some uncertainty regarding this method's ability to sample all isocyanates potentially adhering to the surface in question, and, as mentioned in the previous paragraph, some doubt as to the necessity of knowing the exact quantity of isocyanates present.

3.3.4 Method for assessing isocyanates in finished products

Knowledge about the assessment of "free" isocyanates in finished products has advanced over the past 10 years; however, at the time of writing, there was no consensus on a method able to provide reproducible results. Assessment of isocyanates in finished products is therefore still in the realm of research.

3.3.5 Method for assessing biomarkers of exposure

No method for assessing biomarkers of exposure is available at the IRSST. It is nevertheless worth mentioning that the literature does provide information on isocyanate biomarkers of exposure.

Concentrations of MDI metabolites, such as methylene dianiline (MDA), are found in the plasma and urine of workers exposed to the products of thermal degradation of MDI-based polyurethane. Biological monitoring has several limitations, in particular the half-life of MDI metabolites in plasma, which is several weeks. Biological monitoring of this sort gives a measurement of exposure over a long period. TDI and HDI metabolites, namely toluene diamine (TDA) and hexamethylene diamine (HDA), can be sampled at the end of a work shift, since they are more rapidly eliminated from the body. Since biomarkers do not seem to correlate well with exposure levels, biological monitoring may be more useful as a means of confirming rather than measuring exposure, especially dermal exposure.

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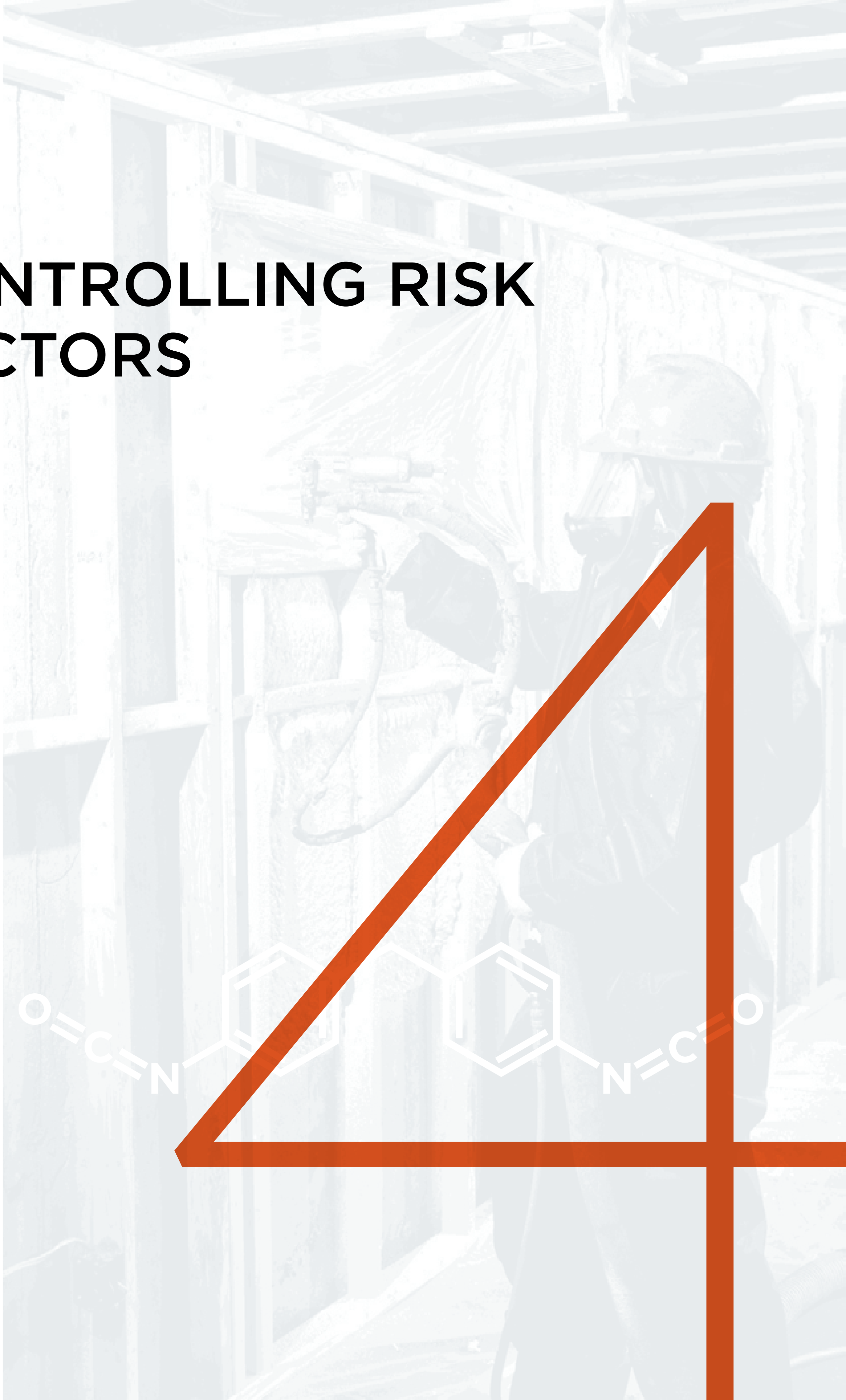
CONTROLLING RISK FACTORS



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CONTROLLING RISK FACTORS

Chemical hazards must be identified (in the Anticipation and Recognition stages) and then evaluated (Evaluation stage). With isocyanates, minimum exposure (EM) is key, and plant engineering for EM from the design phase remains the best prevention option. Let's look nonetheless at other measures for reducing worker exposure no matter what the route of entry into the body.

The risk of developing asthma depends on the intensity and duration of exposure, quantified through environmental monitoring (ROHS, section 43). Exposure to the causative agent over time is thus known and preventive measures can be introduced if permissible exposure values are exceeded.

The most effective preventive measure is plant engineering in the design phase (of ventilation and processes in particular). Installing equipment is easier at this stage, and often less costly, than re-engineering later when the plant is in production. Ventilation systems must be designed to meet the requirements of the ROHS, particularly section 108.

4.1 SUBSTITUTION AND ELIMINATION

The a priori solution for reducing exposure is to substitute other substances for isocyanates. However, substitution is a multiple-step procedure that does not necessarily lead to a solution applicable in the workplace, for reasons of performance, cost, equipment or technical feasibility. The website called Solub, powered by the IRSST and the Université de Montréal, describes the substitution process step by step (in French only).

Another possible solution is to change the equipment or the work methods. For example, a brush or a roller can be used instead of a spray gun. Or, a high-volume low-pressure (HVLP) spray gun can be used to apply automotive coatings as it increases transfer efficiency and generates fewer aerosols.

If substitution and elimination are impossible (frequently the case with isocyanates), worker exposure must be minimized by other means, such as process isolation and/or confinement.

4.2 VENTILATION

When a process generates chemical contaminants to which a worker could be exposed, the work area must be ventilated. Mechanical ventilation (including local exhaust) must remove substances released, in all forms, during the process. Air flow must be directed from clean areas to those that are contaminated. Workers must be located outside the contaminated areas. Contaminated air must be exhausted outside, far from the fresh air intakes, to ensure it is not reintroduced elsewhere in the facility, as specified in section 108 of the ROHS. The ROHS mentions other requirements of this order in sections 101, 103 and 109. The minimum rate of fresh air changes per hour in certain types of facilities as indicated in Table 4.1 are based on Schedule III of the ROHS.

TABLE 4.1

MINIMUM RATE OF AIR CHANGES PER HOUR

TYPE OF ESTABLISHMENT	MINIMUM RATE OF AIR CHANGES PER HOUR
Paints and varnish industry	4
Plastics and synthetic resins industry	3
Veneer and plywood mills	2
Garage for maintenance and repair	4
Industrial chemical products manufacturing	2
Synthetic textile mills	2
Metal fabricating industries (foundry)	4

Spray booths (link in French only) are designed to prevent airborne substances from spreading throughout the shop and to reduce worker exposure. Spray booths should be kept slightly depressurized, with the exhaust air flow rate higher than the intake flow rate. The ventilation system must operate during the facility's business hours, as stipulated in section 5 of the ROHS. An air flow velocity of 0.5 m/s is suggested. Devices – visual indicators (differential pressure gauge) or audible alarms, for example – can provide qualitative air flow information but are not reliable indicators of the maintenance of ventilation flow. In the automotive industry, curtain systems (link in French only) can be used for prep workstations. Such stations are not airtight, however, and must meet specific requirements to ensure effective ventilation.

After the ventilation system is installed and after any modifications, its performance must be evaluated using the assessment grids (link in French only) developed by the CSST for evaluating the risks in auto body repair operations during which skin contact with or inhalation of isocyanates is possible. In addition, preventive maintenance and filter changes must be carried out according to a regular schedule or as needed.

4.3 ADMINISTRATIVE MEASURES

4.3.1 Personal hygiene and workplace cleanliness

When isocyanate-based products are used, there is a risk of exposure through skin contact. As a result, strict personal hygiene measures are required. The hands and face must be washed regularly throughout the workday (before eating, drinking or smoking), and protective coveralls (of Tyvek® or other materials) must be removed for meals. Emergency drench showers and eyewash stations must be installed in shops and other work areas, especially when there is a risk of splashing. A clean workstation prevents resuspension of particles that the process produces.

The spraying of rigid foam often takes place outside the shop (*in situ*), at the jobsite. Workers assigned to rigid foam spraying are particularly at risk of exposure to isocyanates.

4.3.2 Health surveillance

Secondary prevention measures are designed to detect early indicators of sensitization – before the onset of diseases such as occupational asthma (OA). Not only do health surveillance programs make it possible to collect data, but they also educate workers and encourage implementation of occupational health measures.

4.3.3 Training and information

Anyone working with isocyanate-based products must receive training in how to use and handle them safely. They must understand the nature of the risks of exposure to these substances, and the importance of wearing personal protective equipment (including respiratory protection equipment (RPE), work gloves and work clothes) and of good personal hygiene and safe work practices. The training must include pertinent information from WHMIS (Workplace Hazardous Materials Information System) and eventually from GHS (Globally Harmonized System). It must also cover respiratory protective devices and their maintenance (see Legislation).

4.3.4 Work practices and procedures

Certain work practices put workers at risk. Workers must take care not to place themselves within the aerosol cloud produced when spraying in the shop (coatings) or elsewhere (rigid foam *in situ*). When spraying outside the shop, workers often take their breaks in the cab of the company truck without being able to wash their hands. In addition, other workers should be prohibited access to the area where the spraying takes place (or even to the entire jobsite) during the operation. A portable eyewash unit should be available to all who perform spraying outside the shop. Last, work clothes should be washed on site at the end of each shift.

Areas where isocyanate-based products are used must be restricted to workers who have been informed of the associated risks and are wearing appropriate personal protective equipment (clothing, gloves, supplied-air respirator). Empty containers must be decontaminated and then removed from the work premises, as specified in environmental legislation.

Work procedures describe how to do things at the workstation, including how to change paint booth filters and other filters, how to use the equipment and how to maintain the equipment for optimum efficacy. Keeping the work premises clean is crucial, as contaminated tools and equipment can lead to contamination of the skin, causing dermatitis. Isocyanates, as mentioned, are skin irritants.

4.4 PERSONAL PROTECTIVE EQUIPMENT

When other methods of control cannot be implemented – for technical reasons or because of the delivery lead time, for example – personal protective equipment (PPE) can help reduce exposure. Use of respiratory protective devices (RPDs) does not, however, do away with the obligation to eliminate at the source. When isocyanate-based products are sprayed, a supplied-air respirator must be worn. Note that chemical cartridge respirators are not approved by NIOSH 42 CFR, part 84, according to the *NIOSH Pocket Guide to Chemical Hazards* and the NIOSH Certified Equipment List (CEL), mainly because of their very high odour threshold (e.g., 0.02 ppm for TDI). The respirators recommended by NIOSH depending on exposure are:

1. Up to 0.05 ppm: any supplied-air respirator (SAR) (APF[5] = 10 or more) with possibility of eye protection in case of irritation
2. Up to 0.125 ppm: any continuous-flow supplied-air respirator (AFP = 25) with possibility of eye protection in case of irritation
3. Up to 0.25 ppm: any self-contained breathing apparatus (SCBA) with full facepiece or any supplied-air respirator with full facepiece (AFP = 50)
4. Up to 1 ppm: any supplied-air respirator with full facepiece operated in a pressure-demand or other positive-pressure mode (AFP = 2000)

RPDs must be selected, adjusted, maintained and inspected as required by the regulations in effect and the plant's respiratory protection program. NIOSH recommends different devices depending on airborne isocyanate exposure, that is, isocyanate concentrations above time-weighted averages exposure values (TWAEVs)[6] specified in the ROHS – or at any detectable concentration in the case of isocyanates for which there are no reference values. The following are recommended:

- Any pressure-demand or other positive-pressure SCBA with full facepiece
- Any pressure-demand or other positive-pressure supplied-air respirator with full facepiece and an auxiliary SCBA operated in a pressure demand or other positive-pressure mode.

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[5] APF: Assigned protection factor, or the level of respirator protection that a respirator is expected to provide, according to the U.S. Occupational Safety and Health Administration (OSHA), among others.

[6] Also called TWA, or time-weighted average.

The employer must develop a respiratory protection program and explain it to those concerned. The air used must be breathable air in the meaning of CSA standard Z180.1-00. For example, a supplied-air respirator is recommended for spraying of isocyanate-based products (coatings, varnishes, rigid foams, etc.). The compressed breathing air supplied to such respirators must comply with CSA standard Z180.1-00, *Compressed Breathing Air and Systems* (section 48, ROHS) and must be analyzed at least every six months, except in the case of ambient air supply systems. Analysis results must be recorded and kept for a minimum of five years.

For some tasks, an ambient air pump (link in French only) can be used. The pump must be located in an aerated area. The air collected and pumped to the worker must be free of contaminants, such as carbon monoxide (CO) and solvents, and must have no detectable odour.

Despite these obligations, organic vapour cartridges and a particulate prefilter should be used to protect against isocyanates (HDI, IPDI, TDI) in coatings used for automotive refinishing. The protection factor (link in French only) must be higher than 25. All RPDs used must be approved for the intended use and must be included on the *Certified Equipment List* published by NIOSH.

An organic vapour dual-cartridge respirator provides adequate protection against isocyanates in case of spills for **a maximum of one hour (total time of use of the cartridges, all occasions of use combined)**, provided the cartridges were stored in a **hermetically sealed** container between uses. A written cartridge change schedule based on the work to be performed is required.

> The respiratory protection program developed by the employer must include documentation on the RPD protection factors recommended for tasks performed in the plant.

Anyone present during the spraying of isocyanate-containing products must wear a supplied-air respirator. The respirator must also be worn for 15 minutes after the spraying, while the work is being visually inspected. For example, the vapour pressure of the isocyanates (HDI) contained in vehicle coatings is higher than that generated when spraying rigid foam insulation (MDI). This means that a supplied-air respirator is recommended for visual inspection of an automobile coating if the inspection takes place within 15 minutes of spraying.

The choice of eye protection is based on the nature of the work to be performed and the type of RPD used. To protect the eyes and face during spraying, a full facepiece is recommended, or at least air-tight goggles. These protective devices must comply with CSA standard Z94.3.1.09 (link in French only).

Not only must the respiratory tract, the eyes and the face be protected, but all contact with the skin elsewhere on the body must be prevented. According to the Répertoire toxicologique (REPTOX) (link in French only) developed by the Commission de la santé et de la sécurité du travail (CSST), the choice of skin protective equipment depends on the nature of the work to be performed. Latex or cotton gloves do not provide the necessary protection against isocyanates. Gloves of the following materials are recommended:

- Butyl
- Viton®
- Laminate of polyethylene (PE) and ethylene-vinyl alcohol (EVAL): PE/EVAL/PE
- Neoprene and PVC (effective depending on type of activity and its duration

Disposable protective apparel (made of materials such as Tyvek®, Saranex or polyethylene-coated polypropylene) that is hooded and covers the entire body provides satisfactory protection. Other recommended materials include Saranex®23, Chemron, Chemrel®, Dupont® Barricade®, Kappler CPF III® and Kappler Responder®.[7]

Used disposable PPE is considered hazardous waste, as it is isocyanate-contaminated, and must be disposed of in an environmentally safe manner.

4.5 CONTROLLING THE RISK OF DEFLAGRATION

Controlling the risk of deflagration (explosion), particularly in auto body and paint shops, involves eliminating ignition sources (ROHS, sections 50 to 52) and keeping concentrations of inflammable vapours at least 25% below the lower explosive limit (LEL) (ROHS, section 49). Systems for local exhaust of inflammable vapours or gases are also specified and briefly described in section 53 of the ROHS. As stipulated in section 5 of the ROHS, such systems must be operational during the facility's business hours.

4.6 DECONTAMINATION

Decontamination of work surfaces prevents skin exposure to isocyanates via direct contact with contaminated surfaces. Studies show that isocyanates are difficult to neutralize and to remove from certain surfaces. To facilitate cleaning, it is recommended that such work surfaces be painted, as decontaminating solutions are more effective on painted surfaces. When surfactants must be used, a non-ionizing product should be selected (Tergitol® 15-S-5 Surfactant by Union Carbide Corporation), rather than an anionic product. In addition, studies show that ammonia-based solutions are not very effective in neutralizing isocyanates. Best results are obtained with either Isocyanate Decontamination Solution, a commercial product produced by Colormetric Laboratories, Inc. (CLI), or a solution made by mixing grease remover with monoethanolamine (MEA) dissolved in water (Pine-Sol®MEA).[8]

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[7] The list of materials is provided for information purposes only: it is not exhaustive and is not meant to promote any particular material. Mention of a brand does not constitute an IRSST endorsement or performance guarantee.

[8] The IRSST assumes no liability with respect to the products mentioned in this guide, which are listed by way of example only.

During equipment maintenance operations, tanks, drums, etc. should be emptied and washed with an appropriate cleaning product. Workers must receive training for this task and must be properly protected by PPE (RPD, gloves and coveralls). Contaminated clothing (gloves, coveralls), cleaning cloths and resin containers must be disposed of as specified by environmental agencies.

4.7 STORAGE

Products containing isocyanates must be stored as follows:

1. They must be placed in a locked room that is cool and adequately ventilated.
2. They must be kept away from incompatible substances (acids, alkalis and amines).
3. They must be placed in hermetically sealed containers that have been visually inspected for leaks or infiltration.
4. Containers and packaging must be labelled and associated MSDSs must be available.

Access to the storage area must be restricted to authorized personnel trained in procedures for the safe handling of isocyanate-containing products.

Drums and other containers holding isocyanates must not be heated. If the products they contain crystallize due to low warehouse temperatures, the containers must be moved to a warmer, ventilated room. Isocyanate vapours that form during acclimation to the new ambient temperature must be removed from the drum through a valve if necessary.

Established procedures for normal, emergency and maintenance operations must be followed. Local ventilation is required during mixing, weighing, loading, unloading and other operations, or they must be carried out in a well-ventilated space under negative pressure.

A clean and tidy work environment is essential, and equipment must be inspected to ensure it is not damaged. Storage must comply with manufacturer's specifications as indicated on the MSDS. Last, the fire department must be informed of the presence of isocyanate-containing products and of the quantities stored.

4.8 SPILLS

The size of the spill and the environmental conditions at the spill location determine the risk level. For example, a small quantity of lukewarm MDI spilled in an enclosed space is a greater hazard that a larger quantity of cold MDI spilled in an open space. Dry sand or sawdust can be used to contain a spill, but proper decontamination must begin no more than 30 minutes later. In a worst-case scenario (during spill site decontamination for example), the best option is maximum protection (supplied-air respirator, gloves, coveralls of appropriate material). For a scheduled or emergency entry into an area where concentrations are unknown or in a situation immediately dangerous to life or health (IDLH), REPTOX recommends a pressure-demand or other positive-pressure SCBA with full facepiece, or a pressure-demand or other positive-pressure supplied-air respirator with full facepiece and an auxiliary SCBA also operated in pressure demand or other positive-pressure mode. In case of an emergency evacuation, the recommendation is any full facepiece (gas mask) air-purifying respirator equipped with an organic vapour filter, together with an N100 prefilter (in an oil-free setting) or a P100 or R100 prefilter (in a setting that may or does contain oil), mounted at the chin or worn on a belt or harness in front or in back, or any other SCBA appropriate to the situation.

Spills involving isocyanates require immediate action by competent staff trained in spill response. Anyone not trained and mandated for emergency response must leave the premises immediately and inform competent personnel. Product MSDSs include spill response information. Once the spill is controlled through drenching with neutralizer (so it no longer contains free isocyanates), the equipment must be cleaned. When the cleanup is completed, waste and PPE (gloves and coveralls) must be disposed of as required by environmental agencies.

The training program must cover emergency procedures. If there are no competent staff available to take charge of the spill cleanup and decontamination, the premises must be evacuated and an emergency team called in.

The Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs (MDDEFP) offers an environmental emergency service. A response team is available 24/7 across Québec so that all necessary measures can be taken to minimize the impact of emergency situations. This team can be reached at the toll-free number 1 866 694-5454.

If the spill involves a train or a truck, or to obtain additional advice, you can call CANUTEC at 613 996-6666 or *666 from a cell phone, or CHEMTREC at 1 800 262-8200.

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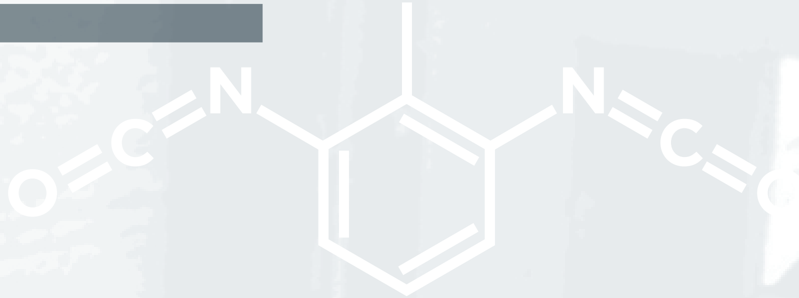
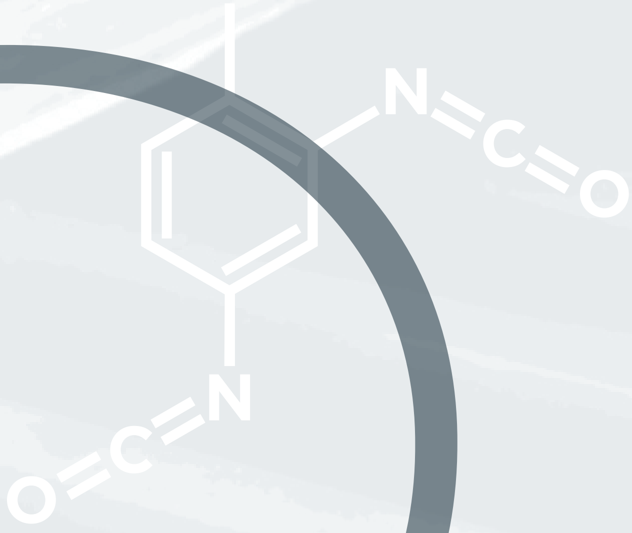
THE INDUSTRIAL HYGIENE APPROACH – EXAMPLES

5





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THE INDUSTRIAL HYGIENE APPROACH – EXAMPLES

This section looks at specific work situations and processes using the approach recommended in this guide for the safe use of isocyanates. In each case, the information gathered in the anticipation, recognition, evaluation (sampling and analysis strategy) and control of risk factors is described.

Note that MSDSs must meet the regulatory requirements of the producing country, which may differ from those in effect in Québec. This could mean that an isocyanate may not necessarily be listed as a product component. The person who consults the MSDS nonetheless generally has access to adequate information regarding the presence and quantity of isocyanates in monomeric and/or oligomeric form in a given chemical product. The MSDS citations for the work situations described below may not correspond with the MSDSs actually used in the plants concerned, as they are meant as pedagogical tools.

To understand the meaning of the designation EM in section 42 and Schedule 1 of the ROHS (exposure must be reduced to a minimum), risk severity analysis is required. Table 5.1 describes some of the steps in a simplified method of risk assessment: a paint shop where vehicles are spray coated is taken as the workplace and the method is based on the approach developed by the INRS (link in French only).

TABLE 5.1

SIMPLIFIED METHOD OF RISK ASSESSMENT (INRS)

STEP	WORKPLACE EXAMPLE
1 ANTICIPATION: INVENTORY OF CHEMICAL AGENTS	
Identify and list chemical agents present or released during the process by gathering available information about health, safety and environmental hazards: ■ Container label ■ MSDS ■ REPTOX ■ Etc.	Use of coating products (primers/base coats, paints, topcoats, etc.) that contain isocyanates (HDI) and solvents
2 RECOGNITION: ANALYSIS OF EXPOSURE CONDITIONS	
Identify hazards and principal exposure factors:	
■ Nature of operations	■ Use of a spray gun
■ Physical form of products	■ Liquid
■ Mode of release	■ Aerosolization and evaporation
■ Quantity used	■ To be evaluated depending on production
■ Route of exposure	■ Inhalation
■ Exposure levels (literature, expert opinion, quantitative measurements, etc.)	■ > 170 µg/m^3 monomer and > 20,000 µg/m^3 oligomer
■ Duration and frequency of exposure	■ To be assessed (e.g.: 5 times/day for 20 minutes)
■ Efficacy of prevention measures	■ Unknown (ventilation, exhaust, etc.)
■ Number of workers concerned	■ To be assessed
3 RISK ASSESSMENT	
Evaluate risk severity	■ Inhalation of allergens (HDI and IPDI) in the form of aerosol or vapour ■ Skin contact ■ Dispersal of contaminants to adjacent areas – if spraying performed in the shop, for example ■ Deflagration
4 CONTROL AND ACTION PLAN	
Match identified risks and prevention measures, looking at the following elements:	
■ Efficacy and feasibility of proposed measures	■ Substitution and process isolation (difficult to implement)
■ Periodic reassessment	■ Local exhaust efficacy (not evaluated? Insufficient?)
■ Medical evaluation	
■ Communication of risks	■ Poster identifying process ■ Access to spraying area restricted to trained and authorized staff ■ Work methods ■ Training and information about hazards, WHMIS and PPE (ROHS, section 47) ■ Wearing of appropriate clothing (see Personal protective equipment) ■ Use of a supplied-air respirator during spraying and for 15 minutes after (during visual inspection)

5

THE INDUSTRIAL HYGIENE APPROACH – EXAMPLES

5.1 CASE A

SPRAY COATING

Photo: Auto-Prévention

Anticipation and recognition

The workplace is an auto body shop where workers use isocyanate-based coatings (primer, topcoat, etc.). The main process of concern is spraying (link in French only), but other tasks, such as preparing the mix and cleaning the equipment when application of the coating is finished, must also be considered.

These types of coatings generally contain aliphatic isocyanates, that is, HDI and/or IPDI. The spraying generates aerosol, and given the vapour pressure of these isocyanates, their presence in vapour form is also anticipated. However, it is also well known that the monomeric isocyanate content of these products is far less than their oligomeric isocyanate content. The following risks can be immediately anticipated:

Exposure through inhalation and skin contact: skin and respiratory pathologies associated with hazardous substances in paints (isocyanates, solvents, pigments, etc.).

Risk of fire and explosion: presence of inflammable solvents in paints and combustible dust clouds in the air (possible explosive atmosphere).

The MSDS of the paint used (Figure 5.1) confirms presence of HDI monomer and oligomers.

FIGURE 5.1

EXTRACT FROM MSDS OF PRODUCT USED IN CASE A

INFORMATION ON INGREDIENTS		
CHEMICAL NAME	CAS NO.	%
Polyisocyanate resin (HDI trimer)	28182-81-2	50 - 75
5-methyl-2-hexanone	110-12-3	7 - 25
N-butyl acetate	123-86-4	< 15
Light aromatic solvent naphtha (petroleum)	64742-95-6	0.25 - 2.5
Hexamethylene diisocyanate	822-06-0	0.1 - 1

HDI OLIGOMERS

HDI MONOMER

Case studies and other scientific publications available also make it possible to anticipate the concentrations observed in similar work settings (Table 5.2). Note that in Québec, the TWAEV for HDI is 34 µg/m^3 (see Table 1 in Appendix 1)

TABLE 5.2

HDI CONCENTRATION RANGES DURING SPRAY PAINTING (FROM DIFFERENT STUDIES)

PROCESS	HDI CONCENTRATION RANGES* (µg/m^3)	
	MONOMER	OLIGOMERS
Car painting (repair)	nd - 30	37 – 58,286
Car painting (repair)	0.003 - 179	0.002 - 26,950
Car painting (spray painting)	nd - 112	nd - 5,494 (NCO**)
Car painting	0.4 - 5.4	2.5 - 728.4 (NCO**)
Car painting	0.004 - 3 1	0.04 - 2,949 (NCO**)
Spray painting	0.7 - 3.8	0.8 - 298

nd: Not detected.

* Monomer results from some studies were converted to standardize the unit of measure.

** NCO means the results are expressed as a function of the isocyanate functional group (µg of NCO/m^3).

Evaluation

The information described above is summarized in Table 5.3 based on the approach presented in the section entitled Sampling and analysis.

TABLE 5.3

ISOCYANATE CHARACTERISTICS, CASE A

CHARACTERISTIC	INFORMATION COLLECTED
Chemical form	0.1 - 1% HDI monomer
	50 - 75% HDI oligomers
Physical form	Vapour (presence of HDI monomer)
	Aerosols (spraying process)
Reaction speed	Slow

Based on this information, the HDI must be evaluated in its oligomeric forms as well as its monomeric form, the oligomers being more abundant and occurring as aerosols. Speed of reaction is generally known to be slow in this type of application.

The IRSST double-filter method (Method 376) is recommended for evaluating inhalation exposure under these circumstances. A maximum sampling duration of 15 minutes will not lead to underestimation and can generally cover all tasks (preparation, spraying and cleaning of the spray gun) associated with application of the coating.

Control

It is important that the operator be protected in a variety of ways during spraying (link in French only), such as a water curtain, a swivel table, a ventilation system or a ventilated enclosure (spray booth, link in French only).

General preventive measures:

- Use spray booths depending on the size of the item to be painted (link in French only)
- Read the product label and the MSDS, especially the precautions for use and storage of the product.
- Wear PPE when performing painting operations (job-rated gloves, work clothes, RPD, etc.)
- Provide training for workers in respiratory protection, hazards present and preventive measures (clean spray guns, prepare mixes in a ventilated mixing room).
- Adapt electrical installations (lighting, room, etc.) based on guidelines for explosive atmospheres.

5.2 CASE B

SPRAY APPLICATION OF POLYURETHANE FOAM INSULATION

Photo: Pierre Charbonneau

Anticipation and recognition

The workplace is a construction site where workers spray isocyanate-based foam insulation on building walls. The process involves spraying two components (isocyanates and a copolymer) which react rapidly together to form a rigid polyurethane foam when mixed.

This type of process generally involves MDI, and spray application of the foam generates aerosols. As MDI has a very low vapour pressure, there will undoubtedly be relatively little in vapour form. Other chemical substances are used in this process in addition to MDI, and these must be taken into account, even though the method under discussion here focuses mainly on exposure to isocyanates. The following risks can be anticipated:

Exposure through inhalation and skin contact: skin and respiratory pathologies associated with hazardous substances in the components (isocyanates, solvents, foaming agents, etc.).

Risk of fire and explosion: presence of inflammable solvents in the components and combustible aerosols in the air (possible explosive atmosphere).

The MSDS of the mix (Figure 5.2) confirms presence of the MDI monomer and MDI oligomers.

FIGURE 5.2

EXTRACT FROM MSDS OF PRODUCT USED IN CASE B

INFORMATION ON INGREDIENTS		
CHEMICAL NAME	CAS NO.	%
Polymethylene polyphenyl polyisocyanate	9016-87-9	45 - 55
Diphenylmethane-4,4′-diisocyanate	101-68-8	45 - 55

MDI OLIGOMERS

MDI MONOMER

Case studies and other scientific publications available also make it possible to anticipate the concentrations observed in similar work settings (Table 5.4). Note that in Québec, the TWAEV for MDI is 51 µg/m^3 (see Table 3 in Appendix 1).

TABLE 5.4

MDI CONCENTRATION RANGES DURING SPRAY APPLICATION OF FOAM INSULATION (FROM DIFFERENT STUDIES)

PROCESS	MDI CONCENTRATION RANGE (µg/m^3)	
	MONOMER	OLIGOMERS
Spray foam trailer	4.4 - 1,460	
Spray application of foam insulation	1.8 - 591	3.1 - 331
	17 - 400	
	70 - 2,050	10 - 1,200

Evaluation

The information described above is summarized in Table 5.5 based on the approach presented in the section entitled Sampling and analysis.

TABLE 5.5

ISOCYANATE CHARACTERISTICS, CASE B

CHARACTERISTIC	INFORMATION COLLECTED
Chemical form	45-55% MDI monomer 45-55% MDI oligomers
Physical form	Aerosols (spraying) Traces of vapour
Reaction speed	Fast

Based on this information, MDI must be evaluated in its oligomeric as well as monomeric forms. Given the spraying process and MDI's low vapour pressure, it is to be anticipated that most of the isocyanate released will be in aerosol form. The chemical reaction is very fast, as it takes places within the aerosols generated (fine droplets of isocyanate and copolymer). Even with a sampling time limited to 15 minutes, the aerosol fraction will be underestimated if a filter method is used. The impinger method (IRSST 376) is recommended for MDI sampling with this type of process, as aerosols and vapours collected can be dissolved and derivatized *in situ*. Based on documented particle size in this type of process, a cassette with a coated filter is not required downstream of the impinger (particles > 2 µm).

Control

There are a number of hazards inherent in this type of work. Here we look only at the chemical risk associated with isocyanates. As the workers will be exposed to aerosols, a number of preventive measures are required:

- Wearing of a supplied-air respirator
- Wearing of hooded protective coveralls of Tyvek® or Barricade® and gloves (link in French only) of nitrile or of polyethylene and ethylene-vinyl alcohol (PE/EVAL/PE) under cotton gloves and a full facepiece or eye protection (e.g., goggles)
- Training for workers in respiratory protection and isocyanate-related risks
- Ensuring of compliance with exclusion zone by posting of a sign announcing the work and mentioning that respiratory and eye protection is mandatory
- No hot work near the exclusion zone
- Removal of coveralls for meals, transportation, etc.
- Prohibition of erection of enclosure on lifting equipment (scaffolds, platforms, etc.)
- Installation of an eyewash station in the cab of the truck

5.3 CASE C

MANUFACTURE OF FLEXIBLE POLYURETHANE FOAM


Photo: AIHA PDC-2000

Anticipation and recognition

The workplace is a plant where flexible polyurethane foam is produced for use in furniture upholstery. Each of two components (isocyanates and copolymer) is pumped from a tank and continuously mixed in a mixing head which delivers the mixture onto a conveyor where the chemicals react to form foam. The conveyor is situated in a ventilated tunnel. Workers who might be exposed are those who transport and cut the finished slabs of foam.

A mixture of TDI isomers is used for this type of process. There is no mechanical dispersion (spraying) in creating the mixture and delivering it to the conveyor. However, because of the vapour pressure of TDI and the temperature of the process, there is vapour diffusion. Other chemical substances are used in this process in addition to TDI, and these must be taken into account, even though the method under discussion here focuses mainly on exposure to isocyanates. The following risks can be anticipated:

Exposure through inhalation and skin contact: skin and respiratory pathologies associated with hazardous substances in the components (isocyanates, solvents, etc.).

Risk of fire and explosion: presence of inflammable solvents in the components.

The MSDS of the isocyanate component used (Figure 5.3) confirms presence of the TDI monomer.

FIGURE 5.3

EXTRACT FROM MSDS OF PRODUCT USED IN CASE C

INFORMATION ON INGREDIENTS		
CHEMICAL NAME	CAS NO.	%
Toluene 2,4-diisocyanate	584-84-9	80
Toluene 2,6-diisocyanate	91-08-7	20

TDI MONOMERS ONLY

Case studies and other scientific publications available also make it possible to anticipate the concentrations observed in similar work settings (Table 5.6). Note that in Québec, the TWAEV for TDI is 36 µg/m^3 (see Table 4 in Appendix 1).

TABLE 5.6

TDI (MONOMER) CONCENTRATION RANGES DURING FOAM MANUFACTURE (FROM DIFFERENT STUDIES)

SUBSTANCE	PROCESS	TDI CONCENTRATION RANGE (µg/m^3)
2,4-TDI 2,6-TDI	**Flexible foam moulding**	0.2 - 7.12 0.02 - 10
TDI	**Flexible foam moulding**	<0.2 - 230 <0.2 - 41

Evaluation

The information described above is summarized in Table 5.7 based on the approach presented in the section entitled Sampling and analysis.

TABLE 5.7

ISOCYANATE CHARACTERISTICS, CASE C

CHARACTERISTIC	INFORMATION COLLECTED
Chemical form	100% TDI monomer
Physical form	Vapour
Reaction speed	Fast

Based on this information, TDI must be evaluated in its monomeric form in the vapour phase. Though the mix reacts quickly to form the polyurethane foam, this is not a problem in terms of sampling – as only unreacted TDI, in vapour-phase, is released into the air. The recommended approach in this case is IRSST double-filter method 376. Without aerosols present, the results will not be affected if sampling time exceeds 15 minutes, as the coated filter will stabilize the isocyanate *in situ*. It is highly recommended that the laboratory be advised to analyze the coated filter only.

Control

- Install local ventilation systems at the workstation and/or enclose the foam-making machine.
- Read the product label and the MSDS, especially the precautions for use and storage.
- Provide training for workers in respiratory protection and the hazards associated with isocyanates.
- In case of insufficient ventilation, wear an RPD and avoid all contact with skin and eyes.

5.4 CASE **D**

APPLICATION OF POLYURETHANE GLUE

Photo: Auto-Prévention

Anticipation and recognition

One of the tasks performed in car repair shops is the installation of windshields with polyurethane glue. The glue is applied with a caulking gun. Isocyanates that might be present are TDI or MDI, depending on the binder used. In the absence of mechanical dispersal, no aerosols are generated. However, TDI vapours may be released to the air, as TDI is very volatile. MDI vapours may be released if the application temperature is high, and these vapours can recondense into very fine aerosols. At ambient temperature, little MDI vapour is released. The following risks can thus be anticipated:

Exposure through inhalation and skin contact: skin and respiratory pathologies associated with hazardous substances in the components (isocyanates, solvents, etc.).

The MSDS of the glue used (Figure 5.4) confirms the presence of MDI monomer and MDI oligomers.

FIGURE 5.4

EXTRACT FROM MSDS OF PRODUCT USED IN CASE D

INFORMATION ON INGREDIENTS			
CHEMICAL NAME	CAS NO.	%	
1,6-hexanediol, adipic acid, diphenylmethane-4,4′-diisocyanate polymer	31075 - 20-4	> 97	**MDI OLIGOMERS**
Diphenylmethane-4,4′ diisocyanate	101 - 68-8	< 3	**MDI MONOMER**

The case studies and other scientific publications available also make it possible to anticipate the concentrations observed in the gluing of automobile parts (Table 5.8). Note that the glue used for this task is not heated. Note as well that in Québec the TWAEV for MDI is 51 µg/m^3 (see Table 3 in Appendix 1).

TABLE 5.8

MDI (MONOMER) CONCENTRATION RANGES USED AS BINDER (FROM DIFFERENT STUDIES)

PROCESS	MDI (MONOMER) CONCENTRATION RANGE (µg/m^3)
Gluing of automobile parts	< 0.2 - 6
Installation of automobile windows	13 - 47.3
	12.6 - 40

Evaluation

The information described above is summarized in Table 5.9 based on the approach presented in the section entitled Sampling and analysis.

TABLE 5.9

ISOCYANATE CHARACTERISTICS, CASE D

CHARACTERISTIC	INFORMATION COLLECTED
Chemical form	MDI monomer < 3%
	MDI oligomers > 97%
Physical form	Vapour
Reaction speed	Slow

Based on this information, only the MDI monomer vapours need to be evaluated. Though there are far more MDI oligomers present in the glue, the process used does not allow for their aerosolization. The recommended approach in the case is IRSST double-filter method 376, and sampling may exceed 15 minutes.

Control

- Read label and MSDS, especially the precautions for use and storage.
- Provide training for workers in respiratory protection and the hazards associated with isocyanates.
- Avoid all contact with skin or eyes.
- Wear skin protection equipment: gloves of nitrile or neoprene.

5.5 CASE E

THERMAL DEGRADATION

Photo: AIHA PDC-2000

Anticipation and recognition

Workers in a body repair shop perform a variety of tasks on the bodies of damaged vehicles: cutting, grinding and welding. Car paints contain aliphatic isocyanates (HDI and/or IPDI).

This type of work causes the temperature of the isocyanate-based (polyurethane) topcoats to increase dramatically, resulting in degradation of the topcoat and formation of a series of monomers, some of them components of the original paint (HDI and IPDI) and others not (MIC, EtIC, PIC and nBIC). Sometimes TDI or MDI from a primer under the other layers of HDI- and/or IPDI-based paint can also be found. Depending on the mechanical dispersion and the temperature reached, release of vapours and particles containing isocyanates must also be considered. The following risks are to be anticipated:

Exposure through inhalation and skin contact: skin and respiratory pathologies associated with presence of hazardous substances released.

Case studies and other scientific publications available also make it possible to anticipate the concentrations observed in similar work settings (Table 5.10).

TABLE 5.10

ISOCYANATE (MONOMER) CONCENTRATION RANGES IN CASE OF POLYURETHANE THERMAL DEGRADATION (FROM DIFFERENT STUDIES)

SUBSTANCE	PROCESS	ISOCYANATE CONCENTRATION RANGE (µg/m^3)
HDI MIC EtIC 2,4-TDI MDI	**Cutting of auto body: training school**	nd - 1.86 0.6 - 2.83 nd - 0.12 nd - 0.81 0.46 - 4.2
IPDI HDI MIC EtIC 2,4-TDI MDI	**Body shop**	1.36 0.27 1.09 nd 0.44 2.13
HDI MIC 2,4-TDI MDI	**Grinding of auto body: training school**	nd - 0.1 0.17 - 0.3 nd - 0.38 0.46 - 1.47
MIC 2,4-TDI MDI	**Body shop**	0.28 0.3 3.04
Diisocyanates and triisocyanates	**Body shop:** ■ **Grinding** ■ **Welding**	 1.7* (1.1) 16* (0.3)
	Machine shop: ■ **Milling and turning**	 19* (18)

nd:Not detected.
*: Maximum concentration.

Evaluation

The information described above is summarized in Table 5.11 based on the approach presented in the section entitled Sampling and analysis.

TABLE 5.11

ISOCYANATE CHARACTERISTICS, CASE E

CHARACTERISTIC	INFORMATION COLLECTED
Chemical form	Monomer of several isocyanates
Physical form	Vapour and aerosol
Reaction speed	Slow

Documenting the characteristics of isocyanates released under thermal degradation is far more complex than documenting those released in a known industrial process for which exposure information is available. The worker or the OHS professional or technician does not necessarily have thorough knowledge of the degraded material. Table 5.10 shows a broad range of isocyanates that could be present. In addition, determining concentrations with such a diversity of isocyanates is a complex task. A semi-quantitative approach is thus advised in this type of situation, using the IRSST high-sensitivity method (Method 366), which allows simultaneous quantification of monomers, in vapour phase, of the most common isocyanates: HDI, IPDI, TDI and MDI. The results obtained can then be used as a semi-quantitative indicator of isocyanate presence.

Control

The study results presented in Table 5.10 suggest that relatively low exposure to isocyanates is to be anticipated. Minimal exposure remains the goal nonetheless. When engineering measures and modification of work methods are not sufficient to reduce exposure, wearing of regulation-compliant PPE may be required (REPTOX, link in French only).

- Use well-sharpened knives, blades and other cutting tools for cutting, grinding, milling and foam cutting.
- Exhaust vapours and dust locally.
- Clean the work area to remove settled dust.

5.6 CASE F

RELOCATION OF A SENSITIZED WORKER

Anticipation and recognition

A workstation adjoining a room where workers apply paint to airplane parts must be assessed for possible relocation of a worker who is sensitized to isocyanates. The isocyanates in the paint are HDI and IPDI. The paint is applied by spraying and the ventilation of the paint rooms is adequate.

In this type of situation, the traces of isocyanates in the air can potentially spread in the form of vapour (hence in monomeric form) beyond the location where they are used. Anticipated concentration levels are well below the TWAEV, but must nonetheless be assessed, as explained in the section on Effects on health. The following risks can be anticipated:

Exposure through inhalation: an asthma attack will be triggered in sensitized workers.

Evaluation

The information described above is summarized in Table 5.12 based on the approach presented in the section entitled Sampling and analysis.

TABLE 5.12

ISOCYANATE CHARACTERISTICS, CASE F

CHARACTERISTIC	INFORMATION COLLECTED
Chemical form	HDI and IPDI, monomer
Physical form	Vapour
Reaction speed	Slow

Recommended approach for sampling and analysis

Based on this information, HDI and IPDI vapours must be evaluated in monomeric form. Reaction speed is not an issue here, but method detection limit is. The recommended approach is thus IRSST Method 366 (high sensitivity), which is adequate for collection and *in situ* derivatization of isocyanates present in vapour phase. The laboratory assay method has a much lower detection limit (see Table 3.2), which, coupled with a sampling volume of up to 480 L (8 hours at 1 L/min), can provide an MRV nearly 800 times lower than that of the IRSST double-filter method (Method 376) with a volume of 15 L.

Control

Relocation is the method of control for exposure of a sensitized worker. Such workers cannot work in an environment where isocyanates are present.

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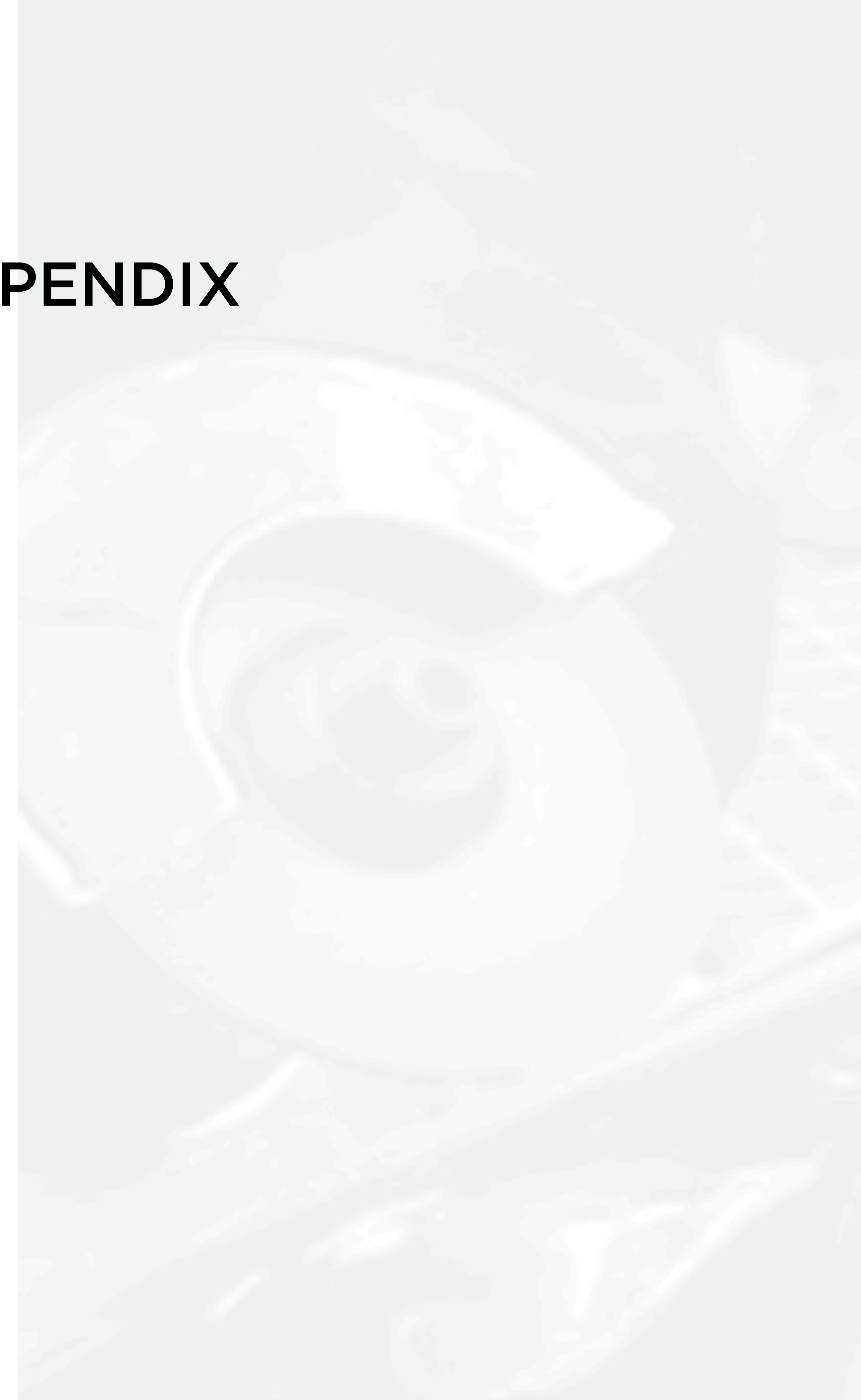
APPENDIX



ISOCYANATE REFERENCE VALUES

TABLE 1

REFERENCE VALUES FOR HEXAMETHYLENE-DIISOCYANATE (**HDI**) (CAS: 822-06-0) – CANADIAN PROVINCES AND ABROAD

PROVINCE OR COUNTRY	TWA		STEL		CEILING		DESIGNATION AND REMARKS		
	ppm	µg/m^3	ppm	µg/m^3	ppm	µg/m^3	SENSITIZER	SKIN	OTHER
Québec	0.005	34					S		EM
Alberta	0.005	30							
British Columbia	0.005				0.01		S		
Ontario	0.005				0.02				
Saskatchewan	0.005		0.015						
Germany	0.005	35	0.005	35	0.005[1]				
Australia[2]		20		70			S		
ACGIH®	0.005						Resp sen		URT irr
United States (NIOSH)	0.005	35			0.020[4]	140[4]			
France	0.01	75	0.02	150			RA		
United Kingdom[2]		20		70			S		
Sweden	0.002	20			0.005[3]	30[3]	S		M
Switzerland[2]		20		20			S		B

In the Québec regulation (ROHS), TWA is referred to as TWAEV and STEL is referred to as STEV.

EM	A substance for which exposure must be reduced to a minimum under section 42 of the ROHS.
Resp sen	Respiratory sensitizer.
URT	Upper respiratory tract.
Irr	Irritation.
RA	Risk of respiratory allergy.
1	15-minute reference period and ceiling.
2	Reference value is for NCO group (monomer and oligomers).
3	5-minute reference period.
4	10-minute reference period.
M	Medical surveillance required to handle the substance.
B	Biological monitoring.
S	Sensitizer.

APPENDIX 1

ISOCYANATE REFERENCE VALUES

TABLE 2

REFERENCE VALUES FOR ISOPHORONE DIISOCYANATE (**IPDI**) (CAS: 4098-71-9) – CANADIAN PROVINCES AND ABROAD

PROVINCE OR COUNTRY	TWA		STEL		CEILING		DESIGNATION AND REMARKS		
	ppm	μg/m^3	ppm	μg/m^3	ppm	μg/m^3	SENSITIZER	SKIN	OTHER
Québec	0.005	45					S		EM
Alberta	0.005	50							
British Columbia	0.005				0.01		S		
Ontario	0.005				0.02				
Saskatchewan	0.005		0.015						
Germany	0.005	40	0.005	46	0.005[1]				
Australia[2]		20		70			S		
ACGIH®	0.005						Resp sen		
United States (NIOSH)	0.005	45	0.02	180				SA	
France	0.01	90	0.02	180			RA		
United Kingdom[2]		20		70			S		
Sweden	0.002	18			0.005[3]	46[3]	S		M
Switzerland[2]		20		20			S		B

In the Québec regulation (ROHS), TWA is referred to as TWAEV and STEL is referred to as STEV.

EM	A substance for which exposure must be reduced to a minimum under section 42 of the ROHS.
Resp sen	Respiratory sensitizer.
RA	Risk of respiratory allergy.
1	15-minute reference period and ceiling.
2	Reference value is for NCO group (monomer and oligomers).
3	5-minute reference period.
M	Medical surveillance required to handle the substance.
B	Biological monitoring.
S	Sensitizer.
SA	Skin absorption.

APPENDIX 1

ISOCYANATE REFERENCE VALUES

TABLE 3

REFERENCE VALUES FOR DIPHENYLMETHANE-4,4’ DIISOCYANATE (**MDI**) (CAS: 101-68-8) – CANADIAN PROVINCES AND ABROAD

PROVINCE OR COUNTRY	TWA		STEL		CEILING		DESIGNATION AND REMARKS		
	ppm	µg/m³	ppm	µg/m³	ppm	µg/m³	SENSITIZER	SKIN	OTHER
Québec	0.005	51					S		EM
Alberta	0.005	50							
British Columbia	0.005				0.01		S	SA	
Ontario	0.005				0.02				
Saskatchewan	0.005		0.015						
Germany		50		50		100	S	SA	
Australia[2]		20		70			S		
ACGIH®	0.005						Resp sen		
United States (OSHA)					0.02	200			
United States (NIOSH)	0.005	50			0.02[4]	200[4]			
France	0.01	10	0.02	200			RA		
United Kingdom[2]		20		70			S		
Sweden	0.002	30			0.005[3]	50[3]	S		M
Switzerland [2]		20		20			S		B

In the Québec regulation (ROHS), TWA is referred to as TWAEV and STEL is referred to as STEV.

EM	A substance for which exposure must be reduced to a minimum under section 42 of the ROHS.
Resp sen	Respiratory sensitizer.
2	Reference value is for NCO group (monomer and oligomers).
3	5-minute reference period.
4	10-minute reference period.
RA	Risk of respiratory allergy.
M	Medical surveillance required to handle the substance.
B	Biological monitoring.
S	Sensitizer.
SA	Skin absorption.

APPENDIX 1

ISOCYANATE REFERENCE VALUES

TABLE 4

REFERENCE VALUES POUR TOLUENE DIISOCYANATE (MIXED ISOMERS) (**TDI**) (CAS: 26471-62-5) - CANADIAN PROVINCES AND ABROAD

PROVINCE OR COUNTRY	TWA STEL		STEL		CEILING		DESIGNATION AND REMARKS		
	ppm	µg/m³	ppm	µg/m³	ppm	µg/m³	SENSITIZER	SKIN	OTHER
Québec	0.005	36			0.02	140	S		EM
Alberta[6]	0.005	40			0.02	100			
British Columbia[6]	0.005				0.01		S		
Ontario[6]	0.005				0.02				
Saskatchewan[6]	0.005		0.02				S		
Germany[6]	0.005	35	0.005	35	0.02	140			
Australia[2]		20		70			S		
ACGIH®[6]	0.005				0.02		Resp sen		
United States (OSHA)[6]					0.02	140			
United States (NIOSH)									
France	0.01	80	0.02	160			RA		
United Kingdom[2]		20		70			S		
Sweden	0.002	14			0.005[3]	40[3]	S		M
Switzerland[2]		20		20			S		B

In the Québec regulation (ROHS), TWA is referred to as TWAEV and STEL is referred to as STEV.

EM	A substance for which exposure must be reduced to a minimum under section 42 of the ROHS.
Resp sen	Respiratory sensitizer.
2	Reference value is for NCO group (monomer and oligomers).
3	5-minute reference period.
RA	Risk of respiratory allergy.
6	Toluene 2,4-diisocyanate (CAS: 584-84-9) and/or toluene 2,6-diisocyanate (CAS: 91-08-7).
M	Medical surveillance required to handle the substance.
B	Biological monitoring.
S	Sensitizer.

ISOCYANATE REFERENCE VALUES

TABLE 5

REFERENCE VALUES FOR DICYCLOHEXYLMETHANE-4,4′ DIISOCYANATE (**HMDI**)[9] (CAS: 5124-30-1) – CANADIAN PROVINCES AND ABROAD

PROVINCE OR COUNTRY	TWA		STEL		CEILING		DESIGNATION AND REMARKS		
	ppm	µg/m³	ppm	µg/m³	ppm	µg/m³	SENSITIZER	SKIN	OTHER
Québec	0.005	54					S		EM
Alberta	0.005	50							
British Columbia	0.005				0.01				
Ontario	0.005				0.02				
Saskatchewan	0.005		0.015						
Australia[2]		20		70			S		
ACGIH®	0.005						Resp sen		URT irr
United Kingdom[2]		20		70			S		
Switzerland[2]		20		20			S		B

In the Québec regulation (ROHS), TWA is referred to as TWAEV and STEL is referred to as STEV.

EM	A substance for which exposure must be reduced to a minimum under section 42 of the ROHS.
URT	Upper respiratory tract.
Irr	Irritation.
2	Reference value is for NCO group (monomer and oligomers).
B	Biological monitoring.
S	Sensitizer.

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[9] Also known as methylene bis(4-cyclohexylisocyanate).

GLOSSARY

ACGIH®	American Conference of Governmental Industrial Hygienists.
Adduct	Different new molecules formed when isocyanates react and chemically bind to proteins.
Alveolitis	An inflammation in the alveoli (small air sacs in the lungs).
Antigen	A substance that is able to trigger an immune reaction or, at the very least, bind specifically with the products of a preceding immune reaction (antibodies or T cell receptors).
AOHS	The Québec Act respecting occupational health and safety (RSQ, c S-2.1).
APF	Assigned protection factor of a respirator.
Asthma	Respiratory syndrome caused by inflammation of the bronchi. Symptoms include coughing, wheezing and difficulty breathing.
ASTM	American Society for Testing and Materials.
Bronchial irritation syndrome	A symptomatic asthma condition characterized by bronchial hyperreactivity persisting for at least three months following accidental exposure. Can be defined as a type of asthma cause by inhalation of a substance with irritant properties in high concentration.
Bronchial provocation test	Exposure in a hospital laboratory or the workplace to a causative agent followed by measurement of lung function in response to the agent. The test can also be performed with an irritant, such as metacholine.
CANUTEC	The Canadian Transport Emergency Centre operated by the Transportation of Dangerous Goods (TDG) Directorate of Transport Canada.
Carcinogenic	Said of a substance that can cause cancer.
CAS	The CAS number or CAS registry number of a chemical, polymer, biological sequence or alloy is its unique registration number in the databank of the Chemical Abstracts Service (CAS), a division of the American Chemical Society (ACS).
CCOHS	Canadian Centre for Occupational Health and Safety.
CHEMTREC	The CHEMical TRansportation Emergency Center, a U.S. emergency response organization in charge of road or rail hazardous spills.
Combustion	An exothermic reaction (heat is released) between a combustible (solid, liquid or gas) and an oxidizing agent (often oxygen in the air).
Conjunctivitis	Irritation of the conjunctiva (mucous membrane) of the eye.
CSA	Canadian Standards Association.
CSST	Commission de la santé et de la sécurité du travail (Québec workers' compensation board).
Dermatitis	Inflammatory skin condition.
Dermatosis	Any skin disease.
Diisocyanate	Chemical compound with two isocyanate (NCO) functional groups.
EC	European Commission.
EM	ROHS notation for a substance to which exposure must be reduced to a minimum.

GLOSSARY

Exposure	Contact with a substance (in this case isocyanates) through inhalation, ingestion or contact with skin or eyes. Exposure can be short-term (acute) medium-term or long-term (chronic).
Genotoxicity	Property of certain physical or chemical toxins (genotoxic agents) that damage the genetic information in exposed organisms and causes mutations.
GHS	Globally Harmonized System.
Hapten	A molecule that can react with proteins. Though haptens alone cannot create an immune response, they can bind with proteins that provoke immune responses.
Hazard	Any source of potential damage, harm or adverse health effects on something or someone under certain conditions at work.
IARC	International Agency for Research on Cancer.
Immunogen	Antigen capable of provoking an immune response.
Immunoglobulin	Blood protein with immune properties. There are several classes and subclasses. IgE is associated mainly with diseases such as asthma and hay fever, whereas IgG is associated with the humoral immune response and fighting of infections.
IPCS	International Programme on Chemical Safety.
IRSST	Institut de recherche Robert-Sauvé en santé et en sécurité du travail (Robert-Sauvé Research Institute on Occupational Health and Safety).
ISO	International Organization for Standardization.
Isocyanate	The chemical functional group made up of nitrogen, carbon and oxygen (NCO). Can also be used to designate any compound with at least one NCO group.
Isomers	Two chemical compounds differentiated by the position of some of their groups or functions.
LEL	Lower explosive or explosion limit. The lowest concentration of a substance in air (expressed as a percentage, volume/volume) at which an inflammable or explosive mix can form.
MAMA	9-(N-methylaminomethyl)anthracene.
Monoisocyanate	Chemical compound with only one isocyanate (NCO) functional group.
Monomer	Simple chemical unit. A polymer is formed when many join together.
MOPIP	(1-(2-methoxyphenyl)piperazine
Mutagenicity	Ability of a biological, physical or chemical agent to provoke mutations in the genetic material of cells.
NCO	Isocyanate functional group (N = nitrogen; C = carbon; O = oxygen).
NFPA	National Fire Protection Association.
NIOSH	National Institute for Occupational Safety and Health (U.S. research organization).
NTP	National Toxicology Program.
OA	Occupational asthma.
Oligomer	Chemical compound with several isocyanate NCO functional groups obtained by condensation of several diisocyanate monomers or by incomplete reaction of diisocyanate and copolymer.
PE	Polyethylene.

GLOSSARY

PE/EVAL/PE	Polyethylene/ethylene-vinyl alcohol/polyethylene.
PEV	Permissible exposure value.
Polyisocyanate	See oligomer.
Polymer	Long-chain chemical compound made of the addition of many simpler units.
Polymerization	Chemical reaction where several monomers react together to form a polymer.
Polyol	Chemical compound with more than two alcohol functional groups.
Polyurethane	Urethane polymer. Urethane (carbamate) is any compound produced by the reaction of an isocyanate and an alcohol (including a polyol).
PPE	Personal protective equipment.
ppm	Parts per million, a unit of measure of concentration.
Prepolymer	See oligomer.
Pyrolysis	Thermal decomposition of organic matter. It is the first stage of thermal transformation, after dehydration.
REPTOX	CSST toxicological database.
Risk	The probability that a dangerous event will occur. Danger is the intrinsic property or characteristic of an object, substance, process or situation of having harmful consequences or threatening the health or safety of a worker.
ROHS	Québec Regulation on Occupational Health and Safety.
RPD	Respiratory protection device.
RV	Reference value.
Sensitization	Immunological process whereby an individual becomes hypersensitive to a chemical substance, manifesting an allergic reaction.
STEL	Short-term exposure limit (15 minutes).
STEV	Short-term exposure value.
Teratogenicity	Capability of certain substances (medications and other substances) of producing fetal malformation.
Triisocyanate	Chemical compound with three isocyanate (NCO) functional groups.
TWA	Eight-hour time-weighted average.
TWAEV	Eight-hour time-weighted average exposure value.
Urethane	Chemical group made of nitrogen, hydrogen, carbon and oxygen (R-NH-COO-R).
WHMIS	Workplace Hazardous Materials Information System.
$\mu g/m^3$	Micrograms per cubic metre, a unit of measure of concentration.

LIST OF HYPERLINKS

Air pump	http://autoprevention.qc.ca/docs/FT_C07_pompe-air-2003.pdf (April 2013).
Alberta	http://employment.alberta.ca/documents/WHS/WHS-LEG_ohsc_2009.pdf (April 2013).
AOHS	http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=/S_2_1/S2_1_A.html (April 2013).
Assessment grids	http://www.csst.qc.ca/publications/200/Documents/DC200_343web.pdf (April 2013), French only.
ASTM	http://www.astm.org/ (April 2013).
Australia	http://hsis.safeworkaustralia.gov.au/ (April 2013).
British Columbia	http://www2.worksafebc.com/Publications/OHSRegulation/GuidelinePart5.asp#EL (April 2013).
CANUTEC	http://www.tc.gc.ca/eng/canutec/menu.htm (April 2013).
CCOHS	http://www.ccohs.ca/oshanswers/hsprograms/hazard_risk.html (April 2013).
Checklists	http://www.csst.qc.ca/publications/200/Documents/DC_200_343_1web2.pdf (April 2013).
CHEMTREC	http://www.chemtrec.com/ (April 2013).
Clean Air Regulation	http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=%2F%2FQ_2%2FQ2R4_1_A.htm (April 2013).
Controlled products	http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=3&file=/S_2_1/S2_1R8_A.HTM (April 2013).
CSA standard Z99.3.1.99	http://www.csst.qc.ca/prevention/magazine/2011/printemps/reportages/Pages/vos_yeux.aspx (April 2013), French only.
Curtain system	http://autoprevention.qc.ca/docs/FT_C03_AireApplication.pdf (April 2013), French only.
Fire prevention	http://www.nationalcodes.nrc.gc.ca/eng/nfc/nfc_2010_contents.html (April 2013).
France (INRS)	http://en.inrs http://en.inrs.fr/.fr/ (April 2013).
Germany	http://www.dguv.de/ifa/en/gestis/limit_values/index.jsp (April 2013).
GESTIS	http://www.dguv.de/ifa/en/gestis/stoffdb/index.jsp (April 2013).
GHS	http://www.hc-sc.gc.ca/ahc-asc/intactiv/ghs-sgh/index-eng.php http://www.ccohs.ca/oshanswers/chemicals/ghs.html (April 2013).
GHS pictograms	http://sti.ac-montpellier.fr/IMG/pdf/SGH.pdf (April 2013).
Gloves	http://www.irsst.qc.ca/media/documents/PubIRSST/R-606.pdf (April 2013), French only.
HSE	http://www.hse.gov.uk/pubns/priced/eh40.pdf (April 2013).
IARC	http://www.iarc.fr/index.php (April 2013).
INRS	http://en.inrs.fr/ (April 2013).
ISO	http://www.iso.org/iso/home/standards.htm (April 2013).

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Method	http://www.inrs.fr/accueil/risques/chimiques/evaluation-risques.html (April 2013), French only.
MDHS 25/3 method	http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs25-3.pdf (April 2013).
MSDS	http://www.inrs.fr/accueil/produits/bdd/doc/fichetox.html?refINRS=FT%2046 (April 2013).
NFPA-30, 2012	http://www.nfpa.org/Assets/files/AboutTheCodes/30/FI30-2012.pdf (April 2013).
NFPA-33 2011	http://www.nfpa.org/Assets/files/AboutTheCodes/33/FI33-2011.pdf (April 2013).
NIOSH	http://www.cdc.gov/niosh/topics/isocyanates/ (April 2013) http://www.cdc.gov/niosh/npg/ (April 2013).
NIOSH Pocket Guide to Chemical Hazards	NIOSH Pocket Guide to Chemical Hazards (April 2013).
NTP	http://ntp.niehs.nih.gov/ (April 2013).
Ontario	http://www.e-laws.gov.on.ca/navigation?file=home&lang=en (April 2013).
OSHA	http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=INTERPRETATIONS&p_id=23425&p_text_version=FALSE (April 2013).
OSHA	http://www.osha.gov./pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992 (April 2013).
Paint booth	http://www.inrs.fr/accueil/produits/mediatheque/doc/publications.html?refINRS=ED%20839 (April 2013), French only.
Paint room sizing	http://www.travailler-mieux.gouv.fr/spip.php?page=risque-prevention&id_article=173 (August 2012), French only.
Preventive measures	http://www.asp-construction.org/utilisateur/documents/Guide_polyurethane_anglais.pdf (April 2013).
Quantitative method	http://www.osha.gov/dts/sltc/methods/validated/w4002/w4002.html (April 2013).
Québec Construction Code	https://www.rbq.gouv.qc.ca/en/laws-regulations-and-codes/construction-code-and-safety-code.html (April 2013).
REPTOX	http://www.reptox.csst.qc.ca/ (April 2013).
ROHS, Québec	http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=%2F%2FS_2_1%2FS2_1R13_A.htm (April 2013).
Sampling guide	http://www.irsst.qc.ca/media/documents/PubIRSST/T-15.pdf (April 2013).
Saskatchewan	http://www.qp.gov.sk.ca/documents/English/Regulations/Regulations/O1-1R1.pdf (April 2013).
Size of the item to be painted	http://www.travailler-mieux.gouv.fr/spip.php?page=risque-prevention&id_ article=173 (April 2013), French only.
Solub	http://www.irsst.qc.ca/solub/ (April 2013).
Spraying	http://www.inrs.fr/accueil/produits/mediatheque/doc/publications.html?refINRS=TS721page16 (April 2013), French only. http://autoprevention.qc.ca/docs/FT_C09_Pulverisation-peinture-2003.pdf (April 2013), French only.
Sweden	http://www.av.se/dokument/inenglish/legislations/eng0517.pdf (April 2013).

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Switzerland	http://www.suva.ch/fr/startseite-suva/praevention-suva/arbeit-suva/arbeitsmedizin-suva.htm#grenzwert (April 2013).
Tergitol	http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_00ae/ 0901b803800aea3b.pdf?filepath=surfactants/pdfs/noreg/119-01950.pdf&fromPage=GetDoc (April 2013), French only.
United Kingdom	http://www.hse.gov.uk/pubns/priced/eh40.pdf (April 2013).
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