A GUIDE TO THE SAFE HANDLING OF POLYURETHANE CHEMICALS

POLYURETHANE PREPOLYMERS
MOISTURE CURING MEMBRANES
POLYURETHANE ELASTOMERS
POLYURETHANE FOAMS

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INTRODUCTION

Some of Isothane's products contain chemical substances that are classified as hazardous under current regulations. All of Isothane's products are supplied with a safety data sheet (SDS) which identifies the hazards of each product. These safety data sheets provide information that can be used by customers to aid them in controlling the risks involved with using harmful chemicals.

This guide is intended to provide extra information on the safe handling of polyurethane chemicals and should be read in conjunction with the relevant product safety data sheet.

As the vast majority of Isothane's products are based on polyurethane chemistry the main hazards to be aware of are:

- Exposure to Isocyanates, mostly MDI and TDI.
- The use of solvents in coating products.
- The use of coal tar mixtures is some coating products.
- Spraying of products containing hazardous substances.
- Corrosive and irritant hazards from some liquid products.

1. PRODUCT DESCRIPTION

1.1 Polyurethane Polymers and Moisture Curing membranes are polymers formed by the reaction between di or poly-isocyanates and compounds having a plurality of active hydrogen atoms, giving products with reactive isocyanate (-NCO) groups

1.2 Polyurethane Elastomers are fully reacted linear or branched molecules of high molecular weight made from poly-functional isocyanates and selected molecules containing at least two active hydrogen atoms.

1.3 Polyurethane foams are formed usually from polymeric poly-functional diisocyanates ("ISO") and 'active' hydrogen compounds, as above ("Resin").

NOTE: A variety of poly-functional isocyanates may be used in all three types, the commonest being toluene diisocyanate (TDI), 4.4'-diisocyanato-diphenylmethane (MDI), its fully hydrogenated form H12 MDI and isophoronediisocyanate (IPDI).

2. HAZARDS AND PRECAUTIONS

2.1 General

Fully reacted polyurethanes contain virtually no available –NCO groups attached to the polymer molecules and there is no free monomeric isocyanate present.

Products with unreacted –NCO groups in the molecule may contain very minor amounts of the free isocyanate from which they were synthesised. Such products are the so-called "one-pack moisture curing polyurethanes" and "prepolymers or adducts" for two-pack curing systems such as for films and foams. In general one-pack moisture curing polyurethanes have less available –NCO groups per molecule than prepolymers or adducts, since they usually rely simply on atmospheric moisture, or catalyst such as amine, to cure. When cured, the latter can exhibit a wide range of physical properties e.g. from hard rigid foams to elastomeric membranes.

With the exception of "foam" components and some polyurethane elastomers, these products are usually supplied as solutions in organic solvent, giving rise to many of the hazards common to resin solutions.

The other principle consideration is the nature and concentration of any free isocyanate present. At low levels above the WEL, skin exposure may induce dermatitis and inhalation may lead to respiratory problems; present evidence suggests that these symptoms, however, are cured by removing the cause. A person exposed to excessive free isocyanate concentrations may become sensitised to the chemical and can then be affected by a few molecules in the atmosphere, which is concentrations well below the WEL. Similarly affected are those suffering respiratory ailments such as asthma ***Medical screening of operatives is therefore a necessary routine procedure***.

It must be emphasised that no undue hazard is involved when polyurethanes are handled with care, and so long as appropriately good standard or industrial and personal hygiene are practised.

It therefore follows that ALL PERSONNEL handling isocyanate containing products must be conversant with the hazards and be trained in the recommended normal and emergency procedures outlined in this document.

The above general remarks, and the information that follows, apply to the great majority of polyurethane; if individual grades contain substances that introduce further hazards, that fact will be indicated by the supplier.

2.2 Fire and Explosion

2.2.1 Solvent free products present little or no fire hazard at normal ambient temperatures however once ignited some may burn fiercely.

Cured product dust at sufficient concentrations, however, constitutes a fire and explosion hazard and once ignited will burn fiercely. It is therefore essential that all sources of ignition be removed from storage and working areas, and that smoking be forbidden. Storage and processing areas should be adequately ventilated and a high level of industrial hygiene maintained to prevent accumulation of dust.

Grinding, cutting or milling of the cured products which produces dust of fine particle size, or mixing finely powdered resin, can lead to the generation of static electricity. Equipment for such operations, including that for dust extraction, should be properly earthed. The discharge of static electricity could lead to ignition or explosion of dust/air mixtures or any flammable vapour produced.

Where practicable, all operations should be carried out in enclosed systems. If dust or fumes are liable to escape an adequate exhaust or ventilating system should be provided.

2.2.2 Polyurethane Prepolymers

All of Isothane's prepolymers do not contain any flammable or non-flammable solvents. They are generally classified are harmful due to the small amount of free isocyanate remaining in the products (less than 1%).
As they contain no solvents there are no risks relating to flammable vapours, or fire and explosive hazards.

2.2.3 Two Pack Products

Some of Isothane's systems are available as two pack products, a "RESIN" component A and an "ISO" component B. In many cases the "ISO" component, particularly polymeric MDI, will contain higher concentrations of isocyanate compared to one-pack prepolymers.

Particular care must be taken in preventing contamination of the "ISO" component with moisture, basic materials (such as sodium hydroxide – "caustic soda"), ammonia, primary and secondary amines, acids and alcohols, as fairly violent reaction may result in pressurisation of containers and excessive heat generation.

For more details refer to the individual safety labels and data sheets, and see below.

2.3 Health Hazards

Good industrial and personal hygiene should be observed. Personnel should be told of the nature of the product being handled. AS WITH ANY CHEMICAL PRODUCT, PERSONS KNOWN TO HAVE A HISTORY OF DERMATITIS, SKIN SENSITISATION OR ASTHMA SHOULD NOT WORK IN DIRECT CONTACT WITH POLYURETHANES.

Emergency eye washing facilities must be available close to the point of use. Adequate general washing facilities should be provided. Skin cleansers are also necessary.

2.3.1 *Inhalation*

Cured Product dust can have an irritant effect on the respiratory tract; large amounts may block the air passages. Approved dust masks should therefore be worn where excessive dust is generated.

Areas where polyurethane prepolymers and coatings are handled or processed should be ventilated so that atmospheric concentrations or vapour are within the Workplace Exposure Limits (WELs) of any free isocyanate contained therein. In general, inhalation of solvent vapour can cause dizziness, headache, nausea, vertigo, lack of co-ordination and unconsciousness at high concentrations as well as irritation of the respiratory passages. In some instances chronic exposure could cause narcosis, anaemia, leukaemia and liver enlargement. Discharges from all ventilation and exhaust systems should be carried well clear of the workplace and of any neighbouring people, houses or other buildings. Dust filters or arrestors may be necessary.

WEL Control Limits for atmospheric isocyanate (-NCO) are:

-0.02 mg/m^3, 8hr time weighted average (TWA)

-0.07 mg/m^3, 10min time weighted average (STEL)

Ventilation sufficient to control solvent vapours below their respective WEL's will normally maintain a safe level of isocyanate vapour. Inhalation of isocyanate causes severe coughing, tightness of the chest and laboured breathing. The onset of symptoms may be delayed several hours after exposure may cause sensitisation (see 2.1).

Other isocyanates such as (MDI, H_{12} MDI and IPDI) have lower hazard level when incorporated into polymers. Nevertheless, for complete safety, the same precautions must be observed as for TDI.

The concentration of free isocyanate in a prepolymer is not a sufficient guide to likely atmospheric vapour concentrations. Spray application creates a greater hazard than brushing because of mist or aerosol formation; fast curing favours lower atmospheric concentrations; the use of less solvent, and of higher boiling solvents, in the formulation helps reduce emission of isocyanate vapour. Test sampling or monitoring of atmospheric isocyanate concentration is necessary wherever there is any doubt, although rapid methods do not exist for all isocyanates, especially the aliphatic types. It should be noted that the detection of isocyanates by smell is dangerous as the odour threshold is generally above the control limit although the actual odour threshold will vary from individual to individual.

When working in environments in which the limits are exceeded (e.g. during spraying) a suitable fresh air mask is required. Care should be taken to ensure these are air tight, since leaks may be a problem with, for example unshaven operators.

2.3.2 *Ingestion*

Polyurethane chemicals should not be ingested. The preparation and consumption of food or beverages should not be allowed where these products are handled or processed.

2.3.3 *Skin Contact*

Prolonged contact in any form with the skin may cause localised irritation leading to dermatitis, and must be avoided. The use of barrier cream on exposed areas of skin may assist in minimising dermatitis effects, barrier creams must be removed with a proprietary cleansing agent. Solvents must not be used for washing.

In the case of polyurethane prepolymer solutions, solvent resistant gloves and – if necessary – overalls and boot, should be supplied and worn; the solvents have a defatting action that leaves the skin prone to irritation and dermatitis, and contact with skin must be avoided. Heavy perspiration induced by impervious gloves can itself cause skin infection; it is generally advisable to wear cotton inner gloves as well, and have them laundered frequently to maintain absorbency and suppleness. Overalls should also be laundered frequently.

2.3.4 *Eye Contact*

Dust, polyurethane prepolymers and solutions can have an irritant effect on the eyes. Goggles should be worn wherever dust is generated and cannot be wholly extracted or where there is a danger of splashing. Effective ventilation is required to prevent fume damage to the eyes.

2.4 Hazards of thermal decomposition

When polyurethane prepolymers and their solutions catch fire, the acrid smoke evolved may contain monomeric isocyanate, and therefore entail hazards specific to these (2.1), as well as those general to dense, choking smoke.

3. EMERGENCY ACTION

3.1 Firefighting

All the products described, particularly those containing volatile flammable solvents, burn fiercely giving rise to black, acrid smoke. Because of this, and the noxious or toxic fumes produced by thermal decomposition, self-contained breathing apparatus is necessary when fighting fires in a confined space. Provided there is no danger to personnel, small fires inside buildings can be controlled by the use of sand, or dry chemical foam extinguishers, which should also be used on fires in the open.

Water is not recommended for extinguishing fires, but may be used to cool tanks, containers and drums etc., in the proximity of fires to prevent overheating and consequent explosion or spread of flames. Generally foam, carbon dioxide or dry powder are recommended media for fire fighting.

In cases of large outbreaks, the local fire service should be alerted. The fire may be contained provided personnel are not put at risk. All not engaged in fire fighting should be evacuated from the area.

3.2 Remedial Action and First Aid

When seeking medical assistance, explain the nature of the product involved, with any details from the supplier regarding special hazards.

3.2.1 *Inhalation*

Remove to fresh air, keep warm and if recovery is not rapid SEEK MEDICAL ATTENTION. Apply artificial respiration if necessary.

3.2.2 *Ingestion*

Do not induce vomiting. Then keep warm, at rest, and SEEK IMMEDIATE MEDICAL ATTENTION.

3.2.3 *Skin Contact*

Remove excess with clean cloth. Clean with proprietary cleansing cream and wash with soap and water. On no account use solvent until advised. Remove any contaminated clothing immediately and do not re-use until laundered.

3.2.4 *Eye Contact*

Irrigate immediately with copious quantities of water for at least 10 minutes, and SEEK MEDICAL ATTAENTION.

3.3 Spillage

Spilled solid products present little hazard: care is needed to prevent excessive dust being created during their removal. Spillages of solutions require more care because of the hazards created by the solvents present. For general disposal procedures see Section 6.

Should any product or solution enter the public drains or waterways, the local Water Authority and the Police must be informed immediately.

4. USE

The polyurethane prepolymers and solutions are intended for use in the manufacture of surface coatings (paints, varnishes, printing inks), adhesives, sealants, roofing, flooring binders, insulation foams etc; polyurethane elastomers are also used in moulding and extrusion. The information given here relates to hazards associated with such uses. If the products are to be used for other purposes, the supplier should be consulted.

The user should not assume on the basis of information provided here that all hazards which can occur with these products are identified here, since there are many different applications and methods of processing and the related hazards involved should be determined by the user.

5. STORAGE

Good standards of industrial hygiene should be observed where polyurethane prepolymers and their solutions are stored. Smoking and the preparation or consumption of food and drink must be prohibited.

Liquids should be stored in a cool place, away from sources of ignition and preferably out of direct sunlight. Prepolymers and moisture curing membranes react with moisture in the atmosphere and should be kept in airtight containers, under a blanket of inert gas (e.g. dry nitrogen). If this is not adhered to rigidly, the product will cure with the evolution of carbon dioxide to create pressure in sealed containers.

If a container has become pressurised, relieve carefully either through a bung hole or by boring a small hole in container (full protective clothing including face shield must be worn).

All liquid prepolymers polymerise to some extent on prolonged storage and eventually solidify. This reaction proceeds very slowly at ambient temperatures and does not produce any hazardous by-products.

Powders should be stored in airtight containers and in a dry place. Excessive dust should not be allowed to build up in the area (see 2.2.1).

For bulk storage or products containing flammable solvents, suitable bunded storage should be provided.

All tanks and containers must be appropriately marked, and during transportation they must be marked, designated and documented so that sufficient information on the hazards and emergency procedures is always available.

Storage locations should be chosen so that in the event of fire there is adequate access for firefighting services. It is strongly recommended that users liaise with the local fire officer regarding the provision of firefighting equipment and the fire precautions and emergency procedures to apply; it should be remembered that these products are not water soluble.

6. WASTE DISPOSAL

6.1 Minor Spillage

The minor spillage should be absorbed with sand, swept up and placed in dry containers for disposal.

Spilt “ISO” component (see section 2.2.3) should be neutralised with decontaminant. The best method is to cover the spill with sand or earth and keep moist with decontaminant mixture.

6.2 Large Spillage

Large spillages should be dealt with by sound engineering practice. Evacuate all unnecessary personnel. Operatives exposed to hazard during contaminant clean-up process should wear the appropriate protective clothing and equipment. Use decontaminant if possible. Once the debris has been shovelled into containers, wash area down with large amounts of water. Monitor atmosphere for isocyanate vapour to ensure safe working conditions before permitting work to recommence.

6.3 Disposal

Where large quantities have to be disposed of, landfill or controlled incineration may be carried out with the approval of the Local Authority. Emptied containers retain vapours and therefore present risks of fire, explosion and vapour hazard, therefore they should only be disposed of after consultation with reputable drum reconditioners and/or the appropriate Local Authority.

"ISO" drums (see 2.2.3) may be decontaminated using the solution outlined above in 6.1.

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