

TRAINING MATERIALS FOR THE SAFE USE OF DIISOCYANATES

Requirements of Annex XVII to REACH Regulation (EC) No 1907/2006 (Item 74)

1. CHEMISTRY OF DIISOCYANATES

O = C = N - (R) - N = C = O

where (R) is any aliphatic or aromatic hydrocarbon

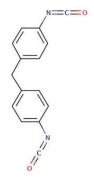
1.1 Diisocyanates (basic compounds)

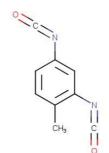
Substance	Abbreviation	CAS
4,4'-methylenediphenyl diisocyanate	4,4'-MDI	101-68-8
2,4-toluene diisocyanate	2,4-TDI	584-84-9
2,6-toluene diisocyanate	2,6-TDI	91-08-7
1,6-hexamethylene diisocyanate	1,6-HDI	822-06-0
isophorone diisocyanate	IPDI	4098-71-9
1,5-naphthalene diisocyanate	1,5-NDI	3173-72-6

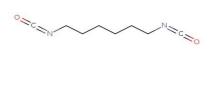




1,6-HDI

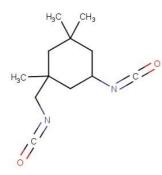


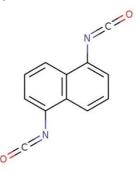




IPDI

1,5-NDI





1.2 Chemical properties

In their pure form, they are generally colourless, white to yellowish-brown, low-melting solids or viscous liquids, readily soluble in non-polar solvents.

Consequences of the high reactivity of the -NCO group:

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a) Contact with water or the presence of moisture degrades them.

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- b) Contact with water, acids or alkalis results in uncontrolled polymerisation (crosslinking), carbon dioxide and heat release (exothermic reactions).
- c) The reaction of diisocyanates with polyols is the basis for the production of polyurethanes (industrial use).
- d) The binding of diisocyanates with biomacromolecules, especially proteins, causes allergenic reactions (reactions with the organism).

2. TOXICOLOGICAL PROPERTIES OF DIISOCYANATES

2.1 Acute toxicity if swallowed

Very low (the material polymerises).

2.2 Inhalation exposure

Acute effect (at higher concentrations): irritation of mucous membranes, eyes.

2.3 Inhalation or dermal exposure

Inhalation or dermal exposure (even at very low concentrations): bronchial asthma, hypersensitivity pneumonitis, allergic rhinitis, conjunctivitis, contact dermatitis. Manifestations: irritating cough, shortness of breath, wheezing, chest tightness, itching and burning of the nose and eyes, watery nasal secretions, itching and redness of the skin. In sensitised individuals, these manifestations can occur even when hygiene limits are observed. Applicable for all diisocyanates and their derivatives:

H317 May cause sensitisation by skin contact.

H334 May cause sensitisation by inhalation.

3. WORKPLACE EXPOSURE LIMIT VALUES

Existing occupational Exposure Limits (OELs) for diisocyanates

Country	TWA-8 hrs	Short term
	[mg.m-3]	[mg.m-3]
Finland	-	0.035 (1)
Ireland	0.02(1)	0.07(1)
Switzerland	0.02	0.02
United Kingdom	0.02	0.07

(1) 15 minutes reference period

Existing occupational Exposure Limits (OELs) for 4,4'-MDI

Country	TWA- 8 hrs [mg.m-3]	Short term [mg.m-3]
Austria	0.05	0.1
Belgium	0.052	
Denmark	0.05	0.1
France	0.1	0.2
Germany (DFG)	0.05 (1)	0,05 (1)
Hungary	0.05	0.05

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Ireland	0.02	0.07 (1)
Poland	0.05	0.2
Romania	-	0.15 (1)
Spain	0.052	-
Sweden	0.03	0.05
USA-NIOSH	0.05	0.2

^{(1) 15} minutes reference period

4. OLFACTORY PROPERTIES OF DIISOCYANATES

Characteristic smell.

Olfactory threshold: 0.4-1 mg/m³ (1–2 orders of magnitude higher than the occupational air limit value).

5. PHYSICAL AND PHYSICOCHEMICAL PROPERTIES OF DIISOCYANATES

5.1 Appearance

- a) 2,4-TDI and 2,6-TDI: yellowish fluids. Melting point 21 °C and 11°C; boiling point 250 °C.
- b) Pure 4,4'-MDI: solid (waxy granules, flakes). Melting point 40 °C.
- c) Polymeric MDI: yellow to brown liquids with varying to oily viscosity
- d) 1,6-HDI: low-viscosity liquid. Boiling point 255 °C.

5.2 Density

>1 g/cm³ (all diisocyanates and derived compounds)

5.3 Solubility in water

They are insoluble, but react with water (not violently): hydrolysis of NCO groups, polymerisation, total elimination of NCO groups = degradation of material, but also loss of toxicity.

5.4 Volatility

- a) 2,4-TDI and 2,6-TDI: 1.4 Pa / 20 °C (saturated vapour at 20 °C: 100 mg/m^3).
- b) Polymeric MDI = liquid containing about 50% of 4,4'-MDI: $3x10^{-4}$ Pa / 20 °C (saturated vapour at 20 °C: 32 μ g/m³).
- c) 1,6-HDI: 7 Pa / 20 °C.

6. EXPOSURE OPTIONS

a) Skin contact: directly through contaminated surfaces.

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- b) Vapour inhalation at normal temperature: 2,4-TDI; 2,6-TDI; 1,6-HDI and not MDI.
- c) Increased vapour production at elevated temperature: at high temperatures also MDI vapours.
- d) Aerosol formation (foaming, spraying): the main exposure route for MDI.
- e) Controlled processes at high temperatures (150 °C): smoke formation.
- f) Thermal stress of PU end products: degradation, reverse release of diisocyanates.



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7. SPECIFICS OF THE USE OF FATRAFIX ADHESIVES IN RELATION TO DIISOCYANATES

7.1 Identification of diisocyanates

Fatrafix FM: 5-20 % 4,4′-MDI (CAS: 101-68-8) **Fatrafix PVC**: 10-30 % 4,4′-MDI (CAS: 101-68-8)

Fatrafix TI:

30-50 % diphenylmethane diisocyanate - isomers and homologues (CAS: 9016-87-9)

10-30 % 4,4'-MDI (CAS: 101-68-8)

< 1% diphenylmethane-2,2'-diisocyanate (CAS: 2356-05-2) < 1% diphenylmethane-2,4'-diisocyanate (CAS: 5873-54-1)

7.2 Use restrictions

Persons who are hypersensitive to diisocyanates may experience allergic reactions when using this product. Persons suffering from asthma, eczema or skin problems should avoid contact with this product, including dermal contact. In conditions without adequate ventilation, this product should not be used without wearing a protective mask with a suitable gas filter (A1 type according to EN 14387).

7.3 The most important acute and delayed symptoms and effects

- a) <u>If inhaled:</u> It may cause allergy or asthma symptoms or breathing difficulties if inhaled. It may cause respiratory irritation. The vapours are heavier than air and can displace or replace air in the breathing zone, thus acting as an asphyxiant. Inhalation of aerosols can have severe toxic effects: a relatively small amount absorbed by the lungs can be fatal. Possible irreversible organ damage. Prolonged or repeated inhalation increases the risk of developing lung diseases.
- b) <u>If on skin:</u> It may cause an allergic skin reaction. Entry into the bloodstream, for example through cuts, abrasions or lesions, causes systematic damage to health.
- c) <u>If in eyes:</u> It causes severe eye irritation. Damage to the eye can occur within 24 hours of contact. Inflammation and redness may occur. Conjunctivitis may occur after prolonged exposure.
- d) <u>If swallowed:</u> Irritation, nausea. Accidental ingestion can seriously damage an individual's health. Ingestion of less than 40 g can be fatal.

7.4 Precautions for safe handling

Use only outdoors or in well-ventilated areas. Use the product only in areas where it does not come into contact with open flames and other sources of ignition. Do not inhale aerosols, avoid contact with skin and eyes. Protect it from direct sunlight. Do not pierce or burn it even after its use. Wash hands and affected body parts thoroughly after handling it. Wear personal protective equipment.

Eye and face protection: Safety goggles with side shields. Contact lenses should not be used.



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Skin protection: Protective gloves (PE/EVAL/PE). Wear canvas or leather gloves when handling sealed cylinders. Alternatively, wear protective overalls well sealed at the neck and wrists. If the product is in contact with the skin, wash the skin thoroughly.

Respiratory protection: AX Filter (AS/NZS 1716 and 1715, EN 143:2000 and 149:2001, ANSI Z88). When working in confined spaces where leakage or breakage of the primary containment is expected (e.g. when changing cylinders), sealed positive-pressure breathing apparatus should be used. Cartridge respirators should never be used for emergency ingress or in areas of unknown vapour concentrations or oxygen content.

7.5 Measures in case of leakage

Remove ignition sources, avoid contact with skin, eyes and clothing. Do not allow to enter the sewer system. Release the pressure in the cylinder by loosening the valve. Spray water or water mist can be used to disperse the vapours. Against spilled diisocyanate, use a decontamination agent (20 parts of diatomaceous earth and 40 parts of a mixture of 8% ammonia, 2% non-ionic wetting agent and 90% water). Let it stand for 24 hours. In the case of major spills, contact the fire department.

7.6 Waste management

Follow the instructions for repurchasing empty FATRAFIX glue canisters, i.e. an empty canister must be punctured (2 holes). Classified as 15 01 04 – Metal packaging. The unpunctured canister cannot be repurchased and is classified under code 15 01 11 – metal packaging containing hazardous material including empty pressure containers.

7.7 Final instructions for Fatrafix diisocyanate adhesives

When storing, handling and disposing of Fatrafix adhesives, follow the instruction manuals. Follow the instructions on the technical data sheets and the safety data sheets.



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