Isocyanates 2.1

What Are Isocyanates?

In simple terms, a **polyurethane** resin is the result of the chemical reaction between a **polyol resin** (also known as "**Part A**") and a **hardener** or **curing agent** (also known as "**Part B**").

The chemically reactive material in the hardener is called the **poly-isocyanate curing agent**, which becomes an integral part of the polyurethane polymer when mixed with the polyol resin. The poly-isocyanate curing agents commonly used in two pack coatings are made from various diisocyanate monomers. In the poly-isocyanate polymerisation process, less than 0.5% remains as **diisocyanate monomer**. When made up into typical two-pack polyurethane coatings, this diisocyanate monomer generally represents less than **0.2% of the total formula**[i].

Although present at low levels, the diisocyanate monomer can pose health risks, if the polyurethane paint is not handled properly.

It is important to note that the risks associated with the diisocyanate monomer should be considered in comparison with risks in using alternative curing agents, and **balanced** with **all other risks** associated with the application of a typical solvent-borne coating.

The use of polyurethane coatings should, in fact, be treated as any industrial process with stringent occupational health and safety guidelines. If the user always followed their respective State Spray Painting Regulations (**Qld**, **NSW**, **ACT**, **Vic**, **Tas**, **SA**, **WA** & **NT**) and wore a well-fitting, positive-pressure, air-fed full-face respirator and overalls, safety shoes and solvent-resistant gloves, then they would not be at any risk at all.

What Are The Potential Hazards Of Isocyanates?

All chemicals have the potential to harm, if used incorrectly. (Even nutritional supplements can cause severe toxic effects if misused.)

However, if a polyurethane paint is handled in accordance with that product's Material Safety Data Sheet and product specifications, **no adverse health effects** are expected.

Symptoms or effects that may arise **if there is uncontrolled exposure to the product or if it is mishandled** are described on the Material Safety Data Sheet as follows:

Ingestion: Swallowing can result in nausea, vomiting and central nervous system depression. If the affected person is showing signs of central system depression (like those of drunkeness) there is greater likelihood of that person breathing in vomit and causing damage to the lungs.

Eye contact: May be an eye irritant.

Skin contact: Contact with skin may result in irritation. A skin sensitiser. Repeated or prolonged skin contact may lead to allergic contact dermatitis.

Inhalation: Material may be an irritant to the mucous membranes of the respiratory tract (airways). Breathing in vapour can result in headaches, dizziness, drowsiness, and possible nausea. Inhaling high concentrations can produce central nervous system depression, which can lead to loss of co-ordination, impaired judgement and if exposure is prolonged, unconsciousness. Respiratory sensitiser. Can cause possible allergic reactions, producing asthma-like symptoms.

Of the above forms of misuse, **inhalation** is the most likely point of entry into the body.

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Risks Associated with Brush and Roller Application

Neither **poly-isocyanate curing agent** nor **diisocyanate monomer** evaporates to any great extent from the polyurethane paint and therefore does not present an inhalation hazard under normal brush and roller application conditions. For more information on solvents, please refer to Dulux® **PC Tech Note 2.2 - Solvents**.

Comparing the vapour pressure[ii] of the **poly-isocyanate curing agent** and the **diisocyanate monomer** with **solvents** (including water) puts the relative risk of inhalation of each into perspective[iii].

Application of polyurethane by brush or roller exposes the applicator to risk of **splash** and **spillage** of wet paint onto **unprotected** areas of the body only, and not to any appreciable amounts of airborne material other than **vapour** which has evaporated out of the wet paint Therefore, the major risks of brush and roller application include **contact** with skin and eyes and **inhalation of vapour**.

Chemical	Vapour pressure (mm Hg at 25°C)	Relative Vapour Pressure (Water = 1)
Poly-Isocyanate	0.000075	0.0000042
Hexamethylene Di Isocyanate	0.025	0.0014
Xylene	8	0.44
Water	18	1
MEK	91	5.06

From the table above, it can easily be seen that the evaporation rate of MEK is five times that of water; xylene is less than half that of water. Both the **poly-isocyanate curing agent** and **diisocyanate monomer** have extremely low vapour pressures, and as these represent only a **small fraction** of the composition of polyurethane paint, it is likely that neglecting to wear a solvent-filter mask will expose the applicator primarily to solvent vapours, rather than any appreciable levels of **poly-isocyanate curing agent** or **diisocyanate monomer under normal circumstances**.

To take a particular example of a high solids polyurethane the table below shows the **relative levels of solvent and diisocyanate** (in this case hexamethylene diisocyanate, HDI) and then **compares** the **vapour pressure** of these components and also shows the **Occupational Exposure Limits** (OEL, the maximum continuous exposure level allowable over an eight hour shift) for each of these components.

Material	Mass per m^2 of applied topcoat (g)	Vapour Pressure (kPa)	OEL (mg/m^3)
HDI	0.048	0.0014*	0.035*
Solvents	45.7	0.2 - 2.0	100 - 480

*ex - Bayer MaterialScience AG material safety data sheet.

The **available HDI** in this case is **three orders of magnitude** (i.e. one thousand times) less than the available solvents. The vapour pressure for the HDI is also approximately three orders of magnitude less than that of the solvents. As the concentration in the air is going to be a product of the available material times its vapour pressure it can be seen that in normal circumstances the solvents will reach their OEL well before the HDI reaches its OEL. That is, it will be necessary to **wear respiratory protection because of the solvents well before** it would be required for the **diisocyanate**.

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Of course in certain circumstances, such as application in confined or poorly ventilated spaces, the concentration of both **solvent vapour** and **diisocyanate** can build up to the extent that allowable exposure levels are exceeded. Consideration needs to be given to the appropriate protective equipment for use in such circumstances.

It remains essential that when applying polyurethanes by brush or roller, that the same precautions are followed as for application of any solvent based paints – these are: **well-fitting, solvent-excluding face masks** (to prevent inhalation of solvent vapour), and **full protective clothing** such as solvent resistant gloves, safety boots, long sleeved tops and overalls (to prevent contact of paint with skin). The exposure risk when applying these coatings by spray is quite different from brush and roller application and so the precautions required for spraying these products are controlled by the specific state regulations previously mentioned.

Risks Associated With Spray Application

Like all paints, waterborne and solvent borne - including polyurethanes - the health risks associated with inhalation increase when the paint is applied by spray. The spray gun creates a **mist** of paint droplets that are small enough to be air-borne and therefore easily **inhaled** during application.

Given that the relative proportion of **diisocyanate monomer** in a droplet is significantly smaller than that of the solvent and solid particle components, it is fair to say that adverse effects arising from spray mist inhalation will be a combination of those from the isocyanate monomer, solvent vapours, pigment particles and other components. In fact it is important to note that, while there are specific health effects associated with the inhalation of poly-isocyanates and diisocyanate monomers which have been previously described, the inhalation of a spray mist from **any** kind of paint system, including water-borne paints, can have adverse health effects and should be avoided.

All respirable particles present inhalation hazards. Even the following common air-borne solids can trigger severe allergic reactions:

- Pollen
- Mould Spores
- Room Deodorisers
- Perfumes
- Saw Dust
- Hay
- Animal Fur
- Certain Food Odours
- Dust Mites
- Asbestos

This is not intended to trivialise the very real risks associated with isocyanates or any other spray applied product, but to put these risks into perspective.

Should I Switch to "Isocyanate-Free" Alternatives?

Alternative two-pack technologies use other curing agents. Whilst they are "isocyanate-free", that does not necessarily mean that they are less hazardous than polyurethanes. In fact, amine-adduct curing agents (the curing agent in epoxies) can produce similar symptoms and effects as isocyanates (if similarly misused).

Given that the coating can be safely used, the primary consideration in choosing a coating system should be whether it can **deliver the protection** and **aesthetics required for the job** – it should be "fit for purpose". Polyurethanes have been the finish coat of choice for much of the past 50 years.[iv]

Unless another technology product is available that can deliver **better performance** and offer **better case histories**, is **demonstrably less hazardous**, and is **not cost prohibitive**, there is **no need to switch**.

Polyurethanes are widely used as finish coats for industrial and architectural high-performance multi-coat systems for long-term protection due to their high gloss and high depth of colour and high UV, abrasion, chemical and water resistance.

The lower (and easier) maintenance requirements, and relatively low initial cost delivers outstanding value over the life cycle of the building or structure.

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How Can I Specify Safe Application of Polyurethanes?

Dulux® Protective Coatings can supply project specifications that take into consideration the issues of isocyanates in polyurethane coatings. Recent developments of the product range now allow us to call up factory (spray applied in contained situation) application for large sections of structure and equipment followed by site touch up that only uses application by brush and roller.

Alternatively, we can accommodate the requirements of those customers who want to apply the total coating at site so that the finish is completely uniform when aesthetics are the major concern.

It is now quite common for Dulux® Polyurethane finishes to be applied to large surface areas of Tank externals by roller and brush methods where spraying is not allowed as paint overspray may impact on nearby areas.

Our Material Safety Data Sheets come with information regarding the safe use of our products. All spray application must comply with respective Australian State Spray Painting Regulations.

Polyurethane Products From Dulux® Protective Coatings

Dulux® Protective Coatings currently manufactures four polyurethanes. These products exhibit outstanding UV, chemical and abrasion resistance, and for this reason are often specified as graffiti-resistant coatings for graffiti-prone areas.

- **Luxathane® R** Spray application
- **Weathermax® HBR** Brush, roller & spray application
- **Durethane® Clear** Spray application
- **Quantum® FX** Spray application

For more information regarding the use of these coatings as graffiti-resistant finishes, please refer to Dulux® Protective Coatings Tech Note 5.9 – Graffiti Resistance.

What Is The Future Of Polyurethanes?

Formulation work continues on polyurethanes using hardeners containing lower levels of unreacted **diisocyanate monomer** to further reduce the risk and hazards associated with isocyanate.

The versatility of polyurethane formulation work allows the possibility of both **higher solids** (lower solvent level) polyurethanes and **waterborne** polyurethanes. Critical success factors will be:

- Ease of spray application to achieve aesthetically pleasing finishes,
- Acceptable practical pot life
- Performance characteristics consistent with current solvent-borne polyurethanes

For more information, please contact the Dulux® Protective Coatings Consultant in your state.

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[i] Please refer to "**Straining at a Gnat and Swallowing a Camel** - Safety And Performance Issues With Two - Part Urethane Finish Coats" ICI Devoe Coatings **http://www.devoecoatings.com/links.do**

[ii] Vapour pressure is a measure of the tendency of a material to form a vapour. The higher the vapour pressure, the higher the potential vapour concentration. In general, a material with a high vapour pressure is more likely to be an inhalation or fire hazard than a similar material with a lower vapour pressure. (Source: CCOHS)

[iii] Table figures from "Polyurethane Coatings - Performance, Quality, Safety" - Mobay Corporation

[iv] ibid - ICI Devoe Coatings Paper