

ISOCYANATES

WHAT ARE ISOCYANATES?

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 formula¹.

Although present at very low levels, the diisocyanate monomer can pose health risks if the polyurethane paint is handled **improperly**. It is important to note that the risks associated with the diisocyanate monomer should be balanced with risks in using alternative curing agents, and with the application of any solvent-borne coating.

The user must always follow their respective State Spray Painting Regulations and wear a well-fitting, positive-pressure, air-fed full-face respirator and overalls, safety shoes and solvent-resistant gloves in order to spray isocyanate containing products safely.

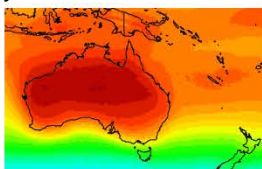
WHAT ARE THE POTENTIAL HAZARDS?

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 relevant Safety Data Sheets, product specifications, and State regulations 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 drunkenness) 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 sensitizer. 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 sensitizer. 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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BRUSH AND ROLLER APPLICATION

Neither poly-isocyanate curing agent nor diisocyanate monomer evaporates to any great extent from the polyurethane paint and therefore do not present inhalation hazards 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 pressureⁱⁱ of the poly-isocyanate curing agent and the diisocyanate monomer with solvents (including water) puts the relative risk of inhalation of each into perspectiveⁱⁱⁱ.

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 solvent 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 solvent**.

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

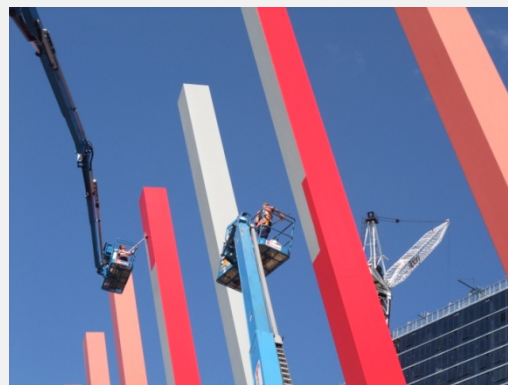
The table above shows that the evaporation rate of MEK is five times that of water; xylene is less than half that of water. Both the poly-isocyanate curing agent and diisocyanate monomer have extremely low vapour pressures, and as these represent only a small fraction of the composition of polyurethane paint, it is likely that an applicator neglecting to wear a solvent-filter mask, will be exposed only to solvent vapours, and virtually zero 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 is necessary to wear respiratory protection primarily because of the solvent vapours and virtually negligible for the diisocyanate.



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Of course in certain situations, such as confined or poorly ventilated spaces, the concentration of both solvent vapour and diisocyanate can exceed allowable exposure levels, so specific protective equipment suitable for these circumstances must be used.

When applying polyurethanes by brush or roller, the same precautions must be followed as for 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 your specific state regulations.

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 polyisocyanates 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

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.

WHAT ABOUT “ISOCYANATE-FREE” COATINGS?

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 equivalent case histories, is demonstrably less hazardous, and is not cost prohibitive, there is no need to switch.



Enclosed environments require special attention to ventilation.



*Safe handling of isocyanates are described in **Safe Work Australia's website**.*



Safe handling of isocyanates always matters, even in well ventilated situations.

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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.

HOW CAN I SPECIFY SAFE APPLICATION OF POLYURETHANES?

Dulux® Protective Coatings can supply project specifications that take into consideration the issues of isocyanate use in polyurethane coatings.

Specifiers should specify factory spray application (spray application in spray booths fitted with extraction units) for large sections and by site touch up by brush and roller where aesthetics are of importance.

Alternatively, Dulux® Protective Coatings supply specifications for total site application using brush and roller, so that the finish is reasonably uniform. Brush and roller application of Dulux polyurethane finishes are now commonly specified for large structures not only for safety reasons, but also where spraying is impractical; such as where paint overspray may land on nearby areas.

Both our product data sheets and our Safety Data Sheets include information regarding the safe use of our products. All spray application must comply with respective Australian State Spray Painting Regulations and Safe Work Australia.

DULUX® POLYURETHANE PRODUCTS

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 about graffiti-resistance, 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 Technical Consultant in your state.



Polyurethanes play an important part of environmentally sustainable design – life cycle assessments have found that transportation of paint is the most significant source of greenhouse gas emissions, whereas the solvents present in the paint transported in the calculation contribute negligibly. Therefore, specifying high performance coatings (regardless of VOC level) is by far the most effective way of reducing greenhouse gas emissions.

ⁱ Please refer to “Straining at a Gnat and Swallowing a Camel - Safety And Performance Issues With Two - Part Urethane Finish Coats” by Mike O'Donoghue, Ron Garrett, V. J. Datta, ICI Devco Coatings

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 Devco Coatings Paper

^v Safe Work Australia “Guide to handling isocyanates” pdf.