Safety bulletin

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Isocyanates from 2-Pack Paints and Use of Polyurethane Resins in Mining

Do you use 2-pack paints, or isocyanate based polyurethane resins (PUR) at your operation? If so, please ensure that you reduce the risk of sensitising workers.

1.0 Isocyanates and painting

Isocyanates are 'respiratory sensitisers' or asthmagens. They can cause a change in people's airways known as the 'hypersensitive state'. A sensitised individual will suffer chest tightness, coughing, wheezing and shortness of breath for several hours after the exposure ceases. Individuals have been so affected that they can no longer work. Refer to www.hse.gov.uk/mvr/experience/isocyanates.htm

Isocyanates used in paint systems can cause health effects via skin contact or when inhaled during paint mixing and spraying. Isocyanate pre-polymers are used in polyurethane paint formulations which, after curing, form durable films. Toluene di-isocyanate (TDI) and diphenylmethane 4, 4-di-isocyanate (MDI) pose a greater health hazard than other isocyanates.

Spray painting with **2-pack paints** produces the highest exposures and has been reported as the main cause of occupational asthma in the United Kingdom. Workplace Health and Safety Queensland also note that isocyanates will "cause occupational asthma in a significant percentage of exposed people".

The fine airborne paint mist is not visible under normal lighting and people may not be aware of the risk. Although brush or roller application of the paint does not create much mist, small amounts of isocyanate vapours released during the process may also be a risk to health. Exposures could also occur during paint mixing, hardening or curing of painted surfaces, and cleaning of spray guns. If not adequately controlled, isocyanate mist and vapours may spread beyond immediate work areas, putting the health of other people, e.g. members of the public, at risk.

Spray painting with two pack paints (even touching up or minor work) should be conducted within a spray booth fitted with effective exhaust capture and filtration systems. It is also important that the ventilation system remains "on" until the paint is fully cured.

1.1 Ways to control the hazard

- Provide induction and training in the health hazards associated with exposure to isocyanates.
- Follow safety instructions provided in the **material safety data sheet (MSDS)** accompanying 2-pack paint and varnish systems. Implement any controls recommended in the MSDS, and ensure that workers have easy access to the relevant MSDS.
- Conduct air monitoring to measure the airborne concentration of isocyanates, and help assess the effectiveness of control measures.

- Wear gloves and a full face air-supplied respirator during spraying. Also wear gloves while cleaning up.
- Ensure the mixing area is well ventilated.
- Arrange a 'designated doctor' to provide ongoing health surveillance for workers who have may have been exposed to significant risk while spraying 2-pack paint and varnish containing isocyanates. A list of designated doctors is available from Workplace Health and Safety Queensland.

For information about hazardous substances in spray painting, refer to the **Spray Painting Guide for Employers and Operators** at www.deir.qld.gov.au/pdf/whs/spraypaint_guide2000.pdf. See also: www.deir.qld.gov.au/workplace/subjects/spraypaint/substances/. Both pages are courtesy of Workplace Health and Safety Queensland.

1.2 Paint mixing and brush or roller application

To minimise vapour levels in the breathing zone of the mixer/painter, carry out this work in a well ventilated mixing/painting area. The UK Health and Safety Executive (HSE) recommends at least 10 air changes per hour with the doors closed, or using a ventilated booth enclosure. Appropriate respiratory protective equipment (RPE) is also recommended for brush/roller work with a coverage area greater than 10 cm^2. Risks from splashing the skin and eyes shall also be reduced by wearing appropriate personal protective equipment (PPE). See www.hse.gov.uk/pubns/indg388.pdf courtesy of the UK HSE.

2.0 Isocyanates and polyurethane resins (PUR)

Polyurethane foam is used extensively in underground coal mines and in some metal mines. The major use is in longwall operations as a strata binder. Polyurethane foam is also used to fill the tyres of free steer vehicles to remove the risk of flat tyres, particularly during periods of intense activity such as longwall moves. Filling tyres with polyurethane is referred to as 'flat proofing'.

Polyurethane is formed by a chemical reaction between a diisocyanate and a polyol in the presence of a catalyst. The diisocyanate may be of various forms; common ones are toluene 2,4-diisocyanate (TDI) and diphenyl methane diisocyanate (MDI). Appropriate additives give the desired properties of the final polyurethane such as resilience, rigidity, hardness, softness, and fire-resistance. Currently in Queensland TDI is used in flat proofing and MDI is used in underground applications. TDI is considered volatile and MDI is considered relatively non volatile. TDI has been banned in many jurisdictions due to its volatility, toxicity and potential for inhalation exposure.

Both one-mix and two-mix polyurethanes are available, however, two-mix polyurethane is the formulation used in the mining industry. One-mix is sold on the domestic market and is familiar to most home handymen.

The chemical reaction that creates polyurethane foam is an exothermic reaction which can take some days to reach completion. Depending on formulation and the presence of contamination, the temperature reached during the setting can vary between 133°C and 198°C. Setting temperatures as high as 300°C have been recorded when using polyurethane in boreholes in explosives applications.

2.1 Flat proofing of heavy duty free steer vehicles

Two-part mix material (one part contains about 6% TDI) is injected into the vehicle's tyres. The process is carried out at tyre-fitting shops off site. Investigation revealed significant problems with lack of training of applicators, lack of knowledge of health hazards and lack of control by material suppliers. This has contributed in the past to a number of incidents in Queensland and NSW.

These defects have now been rectified with the assistance of Workplace Health and Safety Queensland and an awareness campaign which included the Mines Inspectorate issuing a directive to reduce risk under section 166 of the *Coal Mining Safety and Health Act 1999*.

Of concern was that fire fighters or mines rescue personnel generally lacked awareness of the poisonous gases, including hydrogen cyanide (HCN), which are released in the event of a major fire on a vehicle with polyurethane filled tyres.

It should be noted that polyurethane in this application has no fire retardant and spills out from any cuts in the tyre walls. The material would be susceptible to ignition by welding sparks if welding was carried out in close proximity.

2.2 Strata binder

Using polyurethane for strata binding associated with longwall operations accounts for the vast majority of the polyurethane used in Queensland mines. The UK HSE estimates that between 1989 and 2002, about 6,000 tonnes has been supplied from Europe to Australia for use in coal mines.

Polyurethane injection on longwalls is typically carried out by pumping the isocyanate and the polyol through two separate hoses some hundred metres along the longwall face to the location where it is mixed and injected into the strata. Various arrangements are used but each commonly has a delivery pump, located at the main gate, capable of pumping the two components separately to the location where they are required. The two components are taken underground in 20L drums and mixed on the job.

2.3 Health hazards

There are considerable health hazards associated with the use of polyurethane, particularly handling the isocyanate component (TDI or MDI) part of a two part mix. The main health impact is respiratory sensitisation resulting in asthma. Once a person is sensitised, it is almost impossible for them to work with the product without getting a reaction, in this case, an asthma attack.

TDI is on the US National Institute for Occupational Safety and Health (NIOSH) 'Immediately Dangerous to Life and Health' (IDLH) list, see www.cdc.gov/niosh/idlh/idlh-1.html. TDI has an IDLH concentration of 2.5 ppm, while MDI, the polyurethane foams currently used in strata applications in underground coal mines, has an IDLH concentration of 7.5ppm.

The short term exposure limits (STEL) and long term time-weighted-average (TWA) exposure limits protect most workers from adverse health effects. In Australia, isocyanates have exposure limits of STEL 0.07 mg/m^3 and TWA 0.02 mg/m^3 Sen notation (which indicates the substance can cause sensitisation).

Some jurisdictions throughout the world specify even lower limits.

For all isocyanates, transportation, handling, pumping and mixing/injection need to be carefully controlled as does the disposal of any surplus material.

2.4 Health surveillance

Some contracting companies specialise in strata binding using polyurethane for the Queensland underground coal mining industry. The employees of these companies have the potential for significant and on-going exposure to isocyanates.

In the non-mining industry, the *Workplace Health and Safety Act 1995* and associated regulations require frequent and on-going health assessments of these workers. The document 'Guidelines for Health Surveillance [NOHSC; 7039 (1995)]' provides recommendations for the health surveillance necessary to protect the health of workers exposed to isocyanates.

2.5 Fire

There is a history of significant incidents involving polyurethane fires. One incident involved polyurethane foam being ignited by welding sparks creating fires that spread with speed and proved very difficult to extinguish.

The general report on the Kinross Gold Mine fire (South Africa 1988) is that the majority of people died from noxious gases. Tests carried out by the UK HSE on polyurethane foam-filled tyres measured 15 ppm of hydrogen cyanide (HCN) gas given off from the burning material.

HCN is extremely toxic with an Australian TWA peak limitation of 10 ppm, meaning 10 ppm should never be exceeded throughout the work shift, and a NIOSH IDLH level of 50 ppm. HCN also has a "Skin" notation, meaning it can be absorbed through the skin.

Use of a fire retardant in PUR will reduce the risk of fire.

2.6 Spontaneous combustion

The official report into the Michael Colliery fire (Scotland 1968) concluded that the polyurethane was ignited by spontaneous combustion. The report suggests that the polyurethane is such a good insulator that it enhances the coal's propensity to spontaneous combustion and should not be used where coal is prone to spontaneous combustion.

Other concerns emerge from the work carried out by the UK HSE following the Daw Mill Colliery incident (England 2006). When mixing both parts in the correct ratio of 1 to 1, with no water or coal contamination, the maximum curing temperature reached was 133^{o}C. When the mixture is contaminated with water, this rose to 170^{o}C. When the mixing ratio was changed from the recommended 1/1 to 4/1 a maximum temperature of 198^{o}C was reached.

There is an established link between the uncontrolled application of polyurethane and fire, and this was demonstrated by the Westcliff Colliery incident (NSW, December 1986). Observations from a number of experienced mining engineers suggest that there is a connection between using polyurethane as a void filler and spontaneous combustion events. Experiences at North Goonyella in 1996 and anecdotal evidence pertaining to incidents at other mines suggest a connection.

2.7 Controls

Wherever polyurethane is used, a risk assessment must be carried out. Suppliers of polyurethane shall demonstrate that a fire retardant has been added.

It is important that the emergency response management system has identified hazards associated with fire involving polyurethane and that there are adequate controls in place for emergency response.

Rob O'Sullivan
Chief Inspector of Mines
Contact: Kevin Hedges ,Senior Principal Hygienist (North Region), +61 (07) 4799 7766

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