File No: PLC/177

July 2000

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polyurethane Polymer in Polyurethane-Acrylic Dispersion Resin WR-76-5472

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act) and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by the National Occupational Health and Safety Commission which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment and the assessment of public health is conducted by the Department of Health and Family Services.

For the purposes of subsection 78(1) of the Act, copies of this full public report may be inspected by the public at the Library, National Occupational Health and Safety Commission, 92-94 Parramatta Road, Camperdown NSW 2050, between the following hours:

Monday – Wednesday	8.30 am - 5.00 pm
Thursday	8.30 am - 8.00 pm
Friday	8.30 am - 5.00 pm

Copies of the full public report may also be requested, free of charge, by contacting the Administration Coordinator.

Please direct enquiries or requests for full public reports to the Administration Coordinator at:

Street Address: 92 Parramatta Road, CAMPERDOWN NSW 2050, AUSTRALIA
Postal Address: GPO Box 58, SYDNEY NSW 2001, AUSTRALIA
Telephone: (61) (02) 9577 9514
Facsimile: (61) (02) 9577 9465

Director
Chemicals Notification and Assessment

TABLE OF CONTENTS

FULL PUBLIC REPORT

Polyurethane Polymer in Polyurethane-Acrylic Dispersion Resin WR-76-5472

1. APPLICANT

PPG Industries Australia Pty Ltd of McNaughton Rd, CLAYTON, VIC 3169 (ACN 055 500 939) has submitted a Polymer of Low Concern notification statement in support of their application for an assessment certificate for Polyurethane Polymer in Polyurethane-Acrylic Dispersion Resin WR-76-5472.

2. IDENTITY OF THE CHEMICAL

The chemical name, CAS number, molecular and structural formulae, molecular weight, spectral data and details of the polymer composition have been exempted from publication in the Full Public Report.

Trade names: Polyurethane-Acrylic Dispersion Resin WR-76-5472

3. POLYMER COMPOSITION AND PURITY

Precise details of the polymer composition have been exempted from publication in the Full Public Report.

The notified polymer forms part of a core-shell polymer structure. The polyurethane polymer forms the shell, and the acrylic polymer, subject of a concurrent notification NA/791, is formed in situ within this shell. The polyurethane soap is manufactured first, and the acrylic monomers are then added and polymerised while intimately mixed with the polyurethane. No bonds between the acrylic and polyurethane sections are formed, but the two sections of the polymer will be physically interlinked so that they form a single entity. Both components of the core-shell polymer will be crosslinked, so physical interlinking of polymer rings can occur.

Purity (%): 60 % on basis of core-shell polymer solids

Additives/adjuvants:

The notified polymer will be imported in aqueous solution. The identity of additives or adjuvants has been exempted from publication in the Full Public Report, as none are present at above the cutoff for classification of the notified polymer solution as a hazardous substance, and no NOHSC exposure standards apply to these chemicals.

4. PLC JUSTIFICATION

The notified polymer meets the PLC criteria.

5. PHYSICAL AND CHEMICAL PROPERTIES

The polymer is manufactured as an aqueous dispersion and is never isolated. Due to the physical inseparability of the notified polyurethane polymer from the acrylic core, the measured results are for the entire core-shell structure comprising approximately 25 % (w/v) of the polymer dispersion. The properties reported below are variously those of the polymer dispersion and of the core-shell polymer (notified polymer and acrylic polymer subject of NA/791 in a ratio of 60:40), as stated.

Property	Result	Comments
Appearance	milky white low viscosity liquid with little odour	
Boiling point	100°C	polymer dispersion (based on water); notified polymer is not expected to be volatile
Density	1140 kg/m^3 (notified polymer) 1038 kg/m^3 (dispersion)	calculated for notified polymer only
Water solubility	not determined	the core-shell polymer is dispersible in water under basic conditions (see comments below)
Particle size	not applicable	the core-shell polymer only exists as a dispersion in water
Flammability	not flammable	
Autoignition temperature	not determined	
Flash point	91°C	polymer dispersion (based on a minor solvent component)
Explosive properties	not explosive	
Stability/reactivity	stable under normal environmental conditions	
Hydrolysis as function of pH	not determined	the polymer contains ester, polyurethane and carbamate linkages which may undergo hydrolysis under extreme pH conditions; due to the low water solubility, this is unlikely in the environmental pH

		range of between 4 and 9
Partition coefficient	not determined	the notified polymer is expected to be insoluble in water and will largely partition into *n*-octanol rather than water
Adsorption/desorption	not determined	due to its low water solubility, the polymer is expected to readily bind to soils and sediments as it will become becomes viscous and sticky as the water evaporates
Dissociation constant	not determined	the notified polymer contains carboxylic acid functional groups which are partially or completely neutralised with an amine in the dispersion; a small excess of the amine remains in solution

5.1 Comments on physical and chemical properties

A water solubility study was not submitted. The notifier claims that the notified polymer is not soluble but is dipersible in water. The amine is used to provide an anionic charge to the polymer surface and as water is added to the polymer salt it coils into a tight particle bearing the surface charge. This charge provides the dispersion stability. As the concentration of water increases, it is claimed the amine prefers to partition to the water and the polymer becomes more water insoluble. The notifier has provided a literature reference (Eisenberg, 1977) that supports this case for the insolubility of the final emulsion polymer.

6. USE, VOLUME AND FORMULATION

Use:
The notified polymer will be used as a component of a waterborne automotive coating for Original Equipment Manufacture (OEM). The coating will be applied by robot or hand spraying prior to the final assembly of the vehicles. The coating product will be produced in Australia using imported Polyurethane-Acrylic Dispersion Resin WR-76-5472.

Manufacture/Import volume:
The notifier estimates that the import volume will be up to 9 tonnes notified polymer per annum in the first five years of importation, equivalent to 15 tonnes per annum core-shell polymer.

Formulation details:
The notified polymer will be imported as part of a core-shell polymer in an aqueous resin dispersion, WR-76-5472, containing 25 % (w/w) core-shell polymer (15 % notified polymer). The resin dispersion will be reformulated at one site in Australia to produce the paint component, containing up to 20 % (w/w) core-shell polymer (12 % notified polymer). The resin dispersion will be imported in 200 L drums. The finished paint will be stored and transported in 200 L drums.

7. OCCUPATIONAL EXPOSURE

All polymer concentrations are quoted as concentrations of core-shell polymer, rather than notified polymer. After application of the paint, the film will be cured and crosslinked by heating, and overcoated with additional paint layers, and therefore the notified polymer will no longer be separately available for exposure.

Exposure route	Exposure details	Controls indicated by notifier
Formulation		
Laboratory manufacture and testing (3 workers, 8 h/day, 80 days/year)		
dermal 25 % solution	polymer resin dispersion expected to be handled in small quantities under laboratory conditions	exhaust ventilation impervious gloves, coveralls and goggles
Paint make-up (18 workers, 4 h/day, 200 days/year)		
dermal 25 % solution	workers may be exposed to drips and spill of polymer resin dispersion while connecting and disconnecting transfer hoses	exhaust ventilation; enclosed pumping and mixing system impervious gloves, coveralls and goggles
QC testing (3 workers, 4 h/day, 200 days/year)		
dermal 20 % solution	paint expected to be handled in small quantities under laboratory conditions	exhaust ventilation impervious gloves, coveralls and goggles
Drum filling (3 workers, 4 h/day, 200 days/year)		
dermal 20 % solution	workers may be exposed to drips and spill of paint while connecting and disconnecting filling pipes	exhaust ventilation impervious gloves, coveralls and goggles
End use		
Addition of paint to circulation tank (6 workers, 2 h/day, 200 days/year)		
dermal 20 % solution	workers may be exposed to drips and spill of paint while connecting and disconnecting transfer hoses; circulation tank is used for supplying robot spraying system and filling hand spray equipment	enclosed pumping and mixing system impervious gloves, antistatic coveralls and footwear, and eye protection

Hand spray application (20 workers, 8 h/day, 200 days/year)		
dermal, ocular, inhalation 20 % solution	approximately 20 % of paint will be applied by hand in areas with down-draft ventilation; workers will be exposed to a fine mist of paint particles	down-draft spray booth nylon overalls, calico hoods, nylon gloves; cartridge type respirators
Cleaning of spray equipment (6 workers, 2 h/day, 200 days/year)		
dermal 20 % solution	exposure may occur while washing spray equipment with solvents	engineering controls not described impervious gloves, antistatic coveralls and footwear, and eye protection
Transport and storage		
Unloading containers (4-6 workers, 6 h/day, 10 days/year)		
none 25 % solution	handling sealed drums; no exposure expected except in case of accident	none
Transport of drums (4 workers, 4 h/day, 10 days/year)		
none 25 % solution	handling sealed drums; no exposure expected except in case of accident	none

8. PUBLIC EXPOSURE

The notified polymer is not available for sale to the general public. Members of the public may make dermal contact with automobiles coated with products containing the notified polymer. However, exposure will be negligible because the notified polymer will be bound within a cured paint film.

9. ENVIRONMENTAL EXPOSURE

9.1. Release

There is potential for release of the notified chemical during the paint formulation process at the notifier's plant. The notifier estimates that the total waste produced from spills, drum residues and equipment cleaning will be up to 300 kg per annum. This waste will be collected by licensed waste disposal contractors and incinerated.

The paint is applied to automotive surfaces with approximately 75 % efficiency in spray booths with control measures, such as a filtering system and masking materials, in place. This will result in a release of 25 % (2.25 tonne per annum) of the polymer as overspray which will also be disposed of by licensed waste disposal contractors and incinerated.

Cleaning of the spray gun and mixing equipment will generate approximately 300 kg per annum of waste that will be collected and disposed of in the same manner as wastewater from the spray booth.

Some residue will also remain in the 'empty' containers after use. It is estimated that 300 kg per annum of the notified polymer, 3 % of the container contents, will remain as residue in the 'empty' import containers.

9.2. Fate

The waste polymer produced during the reformulation process should be destroyed by incineration after collection by licensed waste disposal contractors. However, if any of the polymer was disposed to landfill it should not be leached out of the soil due to the low water solubility and high molecular weight. It is viscous and sticky when not in the presence of water and excess amine, and should bind to the soils and sediments of the landfill.

In the event of an accidental spillage of the polymer dispersion into the waterways, the polymer will remain suspended in the water fraction until such time as the amine partitions to the water and the polymer gradually becomes insoluble and drops out of solution due to its high molecular weight. It will eventually become associated with the sediments in the rivers and creek beds or ocean floor.

Once applied to the metal panels of heavy vehicles the notified polymer will be incorporated in a hard, durable, inert film and will not present a significant hazard. Any fragments, chips and flakes of the lacquer will be of little concern as they are expected to be inert. The metal panels coated with the polymer are likely to be either recycled for steel reclamation or placed

into landfill at the end of their useful life. When recycled the polymer would be incinerated in the blast furnaces and converted to water vapour and oxides of carbon and nitrogen.

The solid waste generated in the application of the coating will be disposed of by incineration. The 'empty' containers and their residues, which are expected to dry out to a hard inert substance, will also be disposed in this manner. If any of the paint is disposed to landfill, leaching is unlikely, given the expected low solubility of the substance and very high molecular weight. Under these conditions the notified chemical waste would be very slowly degraded to gases such as carbon dioxide through the agency of abiotic and bacteriological processes.

Mixing containers and spray equipment will be washed with solvent that is collected and sent for incineration.

The polymer is not expected to cross biological membranes, due to the anticipated low solubility and high molecular weight, and as such should not bioaccumulate (Connell, 1990).

10. EVALUATION OF HEALTH EFFECTS DATA

No toxicological data were submitted.

The notified polymer is not classified as a hazardous substance according to the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b). It contains low levels of residual monomers and hazardous impurities.

The notified polymer as manufactured contains a number of additives and adjuvants. It is not classified as a hazardous substance according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b) as none of the ingredients are present at above the cutoffs for classification of the notified polymer as hazardous. No exposure standards apply to the solvents present in the polymer resin dispersion.

11. EVALUATION OF ENVIRONMENTAL EFFECTS DATA

No ecotoxicological data were provided. Minimal release to waterways is expected.

12. ENVIRONMENTAL HAZARD (RISK) ASSSESSMENT

The notified polymer crosslinks with other paint components to form a very high molecular weight stable film that adheres firmly to the primer layer to which it is applied. The notified polymer, as part of this surface coating, will share the fate of the vehicle panel. The paint will slowly deteriorate under the action of UV light, but this is not expected to release the polymer over the useful life of the vehicle surfaces. When the vehicle panel is recycled, the notified polymer would be destroyed through incineration.

Overspray will be captured and disposed of by incineration as will paint residues in empty cans and equipment residues. The notifier estimates that a total of approximately 300 kg/annum of the notified polymer will be released to the environment due to the

reformulation process and 2.85 tonnes/annum from the application process. The paint film will contain the notified chemical as part of a crosslinked polymer matrix. The final fate of the notified polymer will be the same as the final fate of the vehicle. That is either to landfill or to recycling where the polymer will be incinerated to water vapour and oxides of carbon and nitrogen.

In the event of an accidental spillage of the polymer dispersion into the waterways, the polymer will remain suspended in the water fraction until such time as the amine partitions to the water and the polymer gradually becomes insoluble and drops out of solution due to its high molecular weight. It will eventually become associated with the sediments in the rivers and creek beds or ocean floor.

Polymer spilt on land, either during usage or transport, is expected to become immobilised in the soil layer. Contaminated soil can then be collected and disposed of to landfill.

Given the above, environmental exposure and the overall environmental hazard is expected to be low. The notified polymer is not likely to present a hazard to the environment when it is stored, transported and used in the typical manner.

13. HEALTH AND SAFETY RISK ASSESSMENT

13.1. Hazard assessment

The notified polymer will not be introduced in isolation, but always as a component of a core-shell polymer, including an acrylic component which is the subject of a concurrent notification, NA/791. The polyurethane and acrylic polymers will not be chemically connected, but will be physically interlinked and therefore inseparable.

No toxicological information has been provided for the notified polymer and therefore the substance cannot be assessed against the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b). The polymer dispersion WR-76-5472 is not a hazardous substance. The Material Safety Data Sheet (MSDS) for the polymer solution WR-76-5472 lists a number of potential health effects, namely nausea, vomiting and skin, eye and respiratory irritation. These relate mainly to the co-solvents, rather than the notified polymer.

13.2. Occupational health and safety

There is little potential for significant occupational exposure to the notified polymer in the transport and storage of the paint components containing this polymer. There will be exposure during the local production of the paint components, and in the use and disposal of the paints.

During the reformulation processes, the main exposure route for the notified polymer will be dermal. The polymer is not expected to be hazardous by dermal exposure as the high molecular weight will preclude absorption through the skin. Standard protective measures including local exhaust ventilation, coveralls, protective eyewear and impervious gloves used during reformulation and end use should provide sufficient protection against the notified polymer.

The final paint mix, including the pre-prepared paint containing the notified polymer, could contain a wide variety of additional ingredients, which may have human health implications,

once fully mixed. The spraying procedure also produces a dense aerosol of paint particles which would adversely affect human health even in the absence of additional hazardous components. It is also probable that professionals involved in the spray painting industry will use a number of different paint formulations.

For these reasons, the notified polymer must be assessed for the contribution it makes to the hazards associated with use of the spray paints. The presence of many potential and actual hazardous substances in the formulations requires the use of stringent engineering controls, such as a correctly constructed and maintained spray booth, and of a high level of personal protective equipment, such as impermeable overalls and gloves and a full face shield and respirator. The use of the paint containing the notified polymer should be in accordance with the NOHSC *National Guidance Material for Spray Painting* (NOHSC, 1999c). The level of protection from exposure afforded by the standard protective measures will provide adequate protection from the notified polymer, which is likely to be less intrinsically toxic than most of the solvents, pigments and other paint resins.

Once the applied final paint mix has hardened, the polymer will not be separately available for exposure or absorption.

Similar considerations apply in the disposal of the polymer. The wastes containing the notified polymer may be hazardous substances on the basis of the solvent and other resin content, and the precautions used on the basis of these additional materials should be adequate for protection from the notified polymer. In addition, much of the polymer will be crosslinked, hardened and immobilised by the time of disposal.

The notified polymer presents a low hazard to human health, and the control measures required due to the more hazardous components of the products containing the notified polymer will ensure sufficient protection against the notified polymer itself.

13.3. Public health

The notified polymer is not available for sale to the general public and will only be used in automotive paint products. Members of the public may make dermal contact with automobiles coated with paints containing the notified polymer. However, the risk to public health from the notified polymer will be negligible because the notified polymer is bound within a cured paint film from which it is unlikely to be bioavailable.

Based on the use pattern of the notified polymer and its physico-chemical properties, it is considered not to pose a significant hazard to public health.

14. MSDS AND LABEL ASSESSMENT

14.1. MSDS

The MSDS of the notified polymer solution provided by the notifier was in accordance with the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994a). It is published here as part of the assessment report. The accuracy of the information on the MSDS remains the responsibility of the applicant.

14.2. Label

The label for the notified polymer solution provided by the notifier was in accordance with the NOHSC *National Code of Practice for the Labelling of Workplace Substances* (NOHSC, 1994b). The accuracy of the information on the label remains the responsibility of the applicant.

15. RECOMMENDATIONS

To minimise occupational exposure to Polyurethane Polymer in Polyurethane-Acrylic Dispersion Resin WR-76-5472, the following guidelines and precautions should be observed:

- Use of the paint containing the notified polymer by spray application should be in accordance with the NOHSC *National Guidance Material for Spray Painting* (NOHSC, 1999c);

- Safety goggles, chemical resistant industrial clothing and footwear and impermeable gloves should be used during occupational use of the products containing the notified polymer; where engineering controls and work practices do not reduce vapour and particulate exposure to safe levels, an air fed respirator should also be used;

- Spillage of the notified chemical should be avoided. Spillages should be cleaned up promptly with absorbents which should then be put into containers for disposal;

- Good personal hygiene should be practised to minimise the potential for ingestion;

- A copy of the MSDS should be easily accessible to employees.

If products containing the notified chemical are hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b), workplace practices and control procedures consistent with State and territory hazardous substances regulations must be in operation.

Guidance in selection of goggles may be obtained from Australian Standard (AS) 1336 (Standards Australia, 1994) and Australian/New Zealand Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand, 1992); for industrial clothing, guidance may be found in AS 3765.2 (Standards Australia, 1990); for impermeable gloves or mittens, in AS 2161.2 (Standards Australia/ Standards New Zealand, 1998); for occupational footwear, in AS/NZS 2210 (Standards Australia/ Standards New Zealand, 1994a); for respirators, in AS/NZS 1715 (Standards Australia/ Standards New Zealand, 1994b) and AS/NZS 1716 (Standards Australia/ Standards New Zealand, 1994c).

16. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, the Director of Chemical Notification and Assessment must be informed if the polymer characteristics cease to satisfy the criteria under which it has been accepted as a Synthetic Polymer of Low Concern, and secondary notification may be required under subsection 64(1). The Director must be informed if any of the circumstances stipulated under

subsection 64(2) of the Act arise, and secondary notification of the notified polymer may be required. No other specific conditions are prescribed.

17. REFERENCES

Connell D. W. (1990) General characteristics of organic compounds which exhibit bioaccumulation. In Connell D. W., (Ed) Bioaccumulation of Xenobiotic Compounds. CRC Press, Boca Raton, USA.

Eisenberg, A. and King, M. (1977) Ion Containing Polymers – Physical Properties and Structure. Polymer Physics, Vol 2, Academic Press, New York.

National Occupational Health and Safety Commission (1994a) National Code of Practice for the Preparation of Material Safety Data Sheets [NOHSC:2011(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994b) National Code of Practice for the Labelling of Workplace Substances [NOHSC:2012(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1999a) List of Designated Hazardous Substances [NOHSC:10005(1999)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1999b) Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1999c) National Guidance Material for Spray Painting. Australian Government Publishing Service, Canberra.

Standards Australia (1990) Australian Standard 3765.2-1990, Clothing for Protection against Hazardous Chemicals Part 2 Limited protection against specific chemicals. Standards Association of Australia.

Standards Australia (1994) Australian Standard 1336-1994, Eye protection in the Industrial Environment. Standards Association of Australia.

Standards Australia/Standards New Zealand (1992) Australian/New Zealand Standard 1337-1992, Eye Protectors for Industrial Applications. Standards Association of Australia/ Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994a) Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994b) Australian/New Zealand Standard 1715-1994, Use and Maintenance of Respiratory Protective Devices. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994c) Australian/New Zealand Standard 1716-1994, Respiratory Protective Devices. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1998) Australian/New Zealand Standard 2161.2-1998, Occupational protective gloves, Part 2: General requirements. Standards Association of Australia/Standards Association of New Zealand.