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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in HE-76-1788

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Postal Address: GPO Box 58, Sydney 2001, AUSTRALIA Telephone: (61) (02) 9577-9514 FAX (61) (02) 9577-9465

Director

Chemicals Notification and Assessment

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FULL PUBLIC REPORT

Polymer in HE-76-1788

1. APPLICANT

PPG Industries Australia Pty Ltd of McNaughton Rd, CLAYTON, VIC 3169 has submitted a limited notification statement in support of their application for an assessment certificate for Polymer in HE-76-1788.

2. IDENTITY OF THE CHEMICAL

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

Marketing Name: HE-76-1788 Modified Polyolefin Resin

Other Name: PMN 1553

Method of Detection The polymer is characterised by GPC and identified by IR spectroscopy. A reference spectrum has been provided.

The Gel Permeation Chromatography results showed that there were a number of reaction products with different molecular weight distributions present in the notified polymer. A high level (>40%) of oligomers with molecular weight less than 1000 was shown to be present.

3. PHYSICAL AND CHEMICAL PROPERTIES

The polymer is manufactured in solution and is never isolated. The properties reported below are variously those of the resin solution containing the notified polymer at 35 % (crude polymer) in mixed organic solvents and of the notified polymer itself, as stated.

Appearance at 20°C brown solid (polymer)

and 101.3 kPa: pale pink viscous liquid (resin solution)

Boiling Point: 118 – 143°C (for the solution)

Specific Gravity: 1.04 (calculated) for the polymer

Vapour Pressure: the notified polymer is not expected to be volatile

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Water Solubility: < 483 mg/L at ambient temperature (see comments

below)

Hydrolysis as a Function

of pH:

not determined (see comments below)

Partition Co-efficient (n-octanol/water):

 $Log P_{ow} = 1.67$ (see comments below)

Adsorption/Desorption: not determined (see comments below)

Dissociation Constant: no dissociable functional groups are present

Particle Size: not applicable as the polymer is not isolated from

solution

Flash Point: 24°C for the solution

Flammability Limits: Upper Explosive Limit = 7 %

Lower Explosive Limit = 1 % (for the solvent xylene)

Autoignition Temperature: 500°C for the solution (similar to the solvent xylene)

Explosive Properties: the polymer is not expected to be explosive

Reactivity/Stability: the polymer is expected to be stable

3.1 Comments on Physico-Chemical Properties

By analogy with similar polymers, the notifier claims that under normal conditions of use the polymer is not expected to be volatile, and that the boiling point for the solution is expected to be in the range 118-143°C (the boiling point of the solvent).

The only test reports that were provided were for water solubility and n-octanol solubility.

The water solubility was determined via a gravimetric analysis (modified OECD Guideline 105 (Flask Method)). Six solutions of the notified polymer were prepared in buffer and stirred for 24 hours at room temperature. The solutions were then centrifuged for 30 mins, separating the soluble and insoluble layers. 10 mL of the soluble layer from each test sample was removed by pipette. Three aliquots were combined to give two samples for drying, after which they were weighed. A control blank was treated in the same manner. The control blank buffer residue weighed more than one of the test sample residues. Therefore, the water solubility was estimated from only one sample. It was found to be 483 mg/L. The limited sensitivity of the technique should be noted as well as the fact that in the daphnia test a white precipitate was observed in the bottom of the flasks at 100 mg/L, suggesting that the polymer solubility is low, at less than 100 mg/L. As there is a high proportion of low molecular weight species present the water solubility is likely to be due to these rather than the notified polymer itself.

FULL PUBLIC REPORT NA/802 The solubility of the notified polymer in n-octanol was determined via refractive index detection, a modification of OECD Guideline 105. Duplicate samples of 6.9 g of notified polymer and 20 mL of n-octanol were mixed for 24 hours, centrifuged at 39 000 g for 30 minutes, and 2 mL of the supernatant were pipetted into a 10 mL flask and diluted with n-octanol. The sample was then filtered and the notified polymer determined by HPLC. The calculated n-octanol solubilities were 22 400 and 22 900 mg/L (average 22 700 mg/L).

The log P_{ow} value was calculated by the ratio of n-octanol and water solubilities and is likely to be an underestimate, due to the uncertainty of the water solubility.

Because of its low solubility and high partition coefficient, the polymer itself may associate with the organic components of soils and sediments. However, the more soluble monomers and oligomers may be more mobile than the polymer itself, and therefore may not adsorb as strongly to soil or sediments.

No dissociation constant data was provided, as the polymer contains no functional groups which are likely to dissociate.

4. PURITY OF THE CHEMICAL

Hazardous Impurities:

Chemical name: oxirane, 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxy

methylene)]bis-

Synonyms: phenol, 4,4'-(1-methylethylidene)bis-, polymer with

(chloromethyl)oxirane (lowest homologue) bis[4-(2,3-epoxypropoxy)phenylpropane

bisphenol A diglycidyl ether

Weight percentage: 5.6 % in polymer solution (16 % of polymer by weight)

CAS No.: 1675-54-3

Toxic properties: R36/38 Irritating to eyes and skin

R43 May cause sensitisation by skin contact

Additives/Adjuvants:

Chemical name: xylene (mixed isomers)

CAS No.: 1330-20-7

Weight percentage: > 60 % in polymer solution

Regulatory Controls: National exposure standard 80 ppm TWA, 150 ppm

STEL (NOHSC, 1995)

Toxic properties: R20/21Harmful by inhalation and in contact with skin

R38 Irritating to skin

(NOHSC, 1999a)

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Chemical name: 1-butanol

Synonyms: n-butyl alcohol

Weight percentage: < 9 % in polymer solution

CAS No.: 71-36-3

Regulatory Controls: NOHSC exposure standard 50 ppm peak limitation

(skin notation)

Toxic properties: R20 Harmful by inhalation

The notified polymer will be imported in a pre-prepared paint, and will have a number of other additives including pigments.

5. USE, VOLUME AND FORMULATION

The notified polymer will initially be imported as a component of a pre-prepared paint for automotive refinish use, at < 10 % (w/w). It will be imported at < 1 tonne per annum during the first five years. No reformulation will occur in Australia initially, although the polymer solution containing 35 % crude notified polymer may at some later date be imported for local production of the paint.

6. OCCUPATIONAL EXPOSURE

Pre-prepared paints containing the notified polymer will be imported in 1 L steel cans. The notifier has provided no detail on the type of packaging for the overall shipment of imported individual containers or the handling involved in breaking up the shipment into individual containers for dispatch to the customer sites. The individual product containers are not expected to be opened before arrival at the end use site and the likelihood of a spill is low.

The polymer solution for future reformulation will be imported in 200 L steel drums. It will be transferred from the docks by road transport to the reformulation site. No details of warehouse and transport workers involved in handling the notified polymer were provided by the notifier.

Waterfront, transport and warehouse workers are not expected to be exposed to the notified polymer except in the case of an accident involving spillage of the paint or resin solution.

The laboratory development and reformulation into coatings will be carried out at a single site within Australia.

Laboratory Development

The notifier indicated that 3 laboratory workers would be involved in the manufacture and testing of paint. The potential exposure would be for up to 8 hours per day, for up to 20 days per year. Exposure would be by skin contact during the handling of small quantities of the polymer solution and paint. The use of appropriate laboratory ventilation facilities and personal protective equipment such as a laboratory coat and safety glasses would be

expected.

Paint Manufacture

The reformulation of polymer solution into paint components, when commenced, will involve 9 workers for up to 8 hours per day, 30 days per year. Three groups of workers will be involved in the process; in paint mixing, quality control and drum or can filling. The mixers used for preparing the paint will be enclosed and fitted with local exhaust ventilation. Dermal exposure to the polymer will be possible at several points throughout the process; charging the polymer solution into the mixer, removal and testing of quality control samples, and drips and spills during the paint filtration and filling. The formation of aerosols during the high speed mixing will be unlikely because of the viscosity of the mixture.

The mixing and filling will be carried out under local exhaust ventilation to prevent exposure to the solvents. Workers will wear impervious gloves, coveralls and goggles, with additional personal protective equipment being used as required.

Paint Application

The notifier estimates that as many as 1000 spray painters in up to 1000 establishments across Australia could be exposed to the notified polymer. The exposure is estimated to be for up to 4 hours per day, on a daily basis. The notifier has not indicated whether the paint is further diluted or mixed prior to use. The typical procedure for spray painters is described below.

The spray painters who will be exposed to the notified chemical will be fully TAFE trained. Typically the spray painter will measure the appropriate amounts of the different components required in a particular formulation into an open container and pour this mixture into a spray gun. The spraying of the automobile will be carried out in a laminar flow downdraft spray booth which is designed to rapidly remove aerosol particles and solvent vapour from the atmosphere. Several possible booth designs may be used. In a dry floor booth, the overspray will be collected in filters contained in the floor of the booth; any unremoved particulates will reach the exhaust stack with the solvent vapours. In a wet floor booth, overspray will collect in a pool of water below the grill floor or in a wet scrubber in the exhaust and will be removed with a filter. The residual solids will be disposed of to secure landfill. The spray booths are subject to AS/NZS/4114.1:1995 Spray Painting Booths – Design, Construction and Testing and AS/NZS/4114.1:1995 Spray Painting Booths – Selection, Installation and Maintenance.

Residual paint mixture is likely to be washed from the equipment manually, and the washings disposed of by licensed waste disposal contractors.

Once the final paint mixture has dried, the notified polymer will be irreversibly bound within the cured matrix and covered by several additional paint layers, and will not be separately available for exposure to workers.

Spray painters will wear appropriate personal protective equipment at all times; impervious gloves and anti-static flame retardant overalls while mixing the paint, and, in addition, a full face shield and respirator conforming to AS/NZS1715 and AS/1716 while inside the spray booth.

7. PUBLIC EXPOSURE

The notified polymer will enter the public domain only in the form of cured paint films on automobiles. This paint film will contain the polymer in a crosslinked unreactive form which will not be bioavailable. In addition, the notified polymer will be covered by several additional paint layers before it enters the public domain.

8. ENVIRONMENTAL EXPOSURE

8.1 Release

There is the potential for spills to occur during transport, storage, manufacture and use. The amount lost in this manner is expected to be minor. Spills during manufacturing will be contained by bunding and go to the on-site treatment plant.

Waste streams in the manufacturing process all go to on-site treatment (the "Dusol" process). In this process any paint or resin is dissolved and converted to an inert solid which is then disposed of to landfill. It is estimated that up to 10 kg of waste will be generated per year from this process.

At user sites the biggest source of waste will be the spray application with up to 70 % ending up as overspray. This overspray will be captured within the booth or in the filters of the exhaust ventilation system. It is estimated that up to 350 kg of waste will be generated per year, from the cleaning of spray guns, mixing equipment, spray booths and filters and from masking materials such as kraft and newspaper. This waste will be sent to landfill after treatment by licensed waste contractors.

It is estimated that there will be a 2 % residue in containers, ie up to 10 kg per year. This residue will be allowed to dry then disposed of to landfill.

8.2 Fate

The final fate of the polymer will be the same as the coated article, ie either recycled or disposed of to landfill. During the recycling process the coating (incorporating the polymer) will either be removed and become part of a solid or sludge waste that will go to landfill or incineration, or it will be destroyed by smelting. Incineration of the coating would emit noxious fumes including oxides of carbon. Over the life of the car (average 20 years) there will be slow deterioration of the coating/paint due to exposure to UV light.

The solid wastes generated in the manufacturing (up to 10 kg per year) and application of the paint (up to 360 kg by year 5) will be disposed of to landfill. Leaching of the polymer from landfill is unlikely since the majority of the polymer will be present within a cured inert paint matrix. When the raw polymer is disposed to landfill, the polymer itself is likely to adsorb to soil, but the monomers and oligomers present may have a lesser affinity for soil and may leach.

The polymer is not expected to cross biological membranes due to its high molecular weight and large size, and therefore should not bioaccumulate (Connell, 1990), however the

monomers and oligomers may cross biological membranes and bioaccumulate (Boethling, 1997).

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Acute Toxicity

9.1.1 Oral Toxicity (Edgar, 1997)

Species/strain: rat/Sprague-Dawley

Number/sex of animals: 5/sex

Observation period: 15 days

Method of administration: gavage, test material dissolved in maize oil; dose

2000 mg/kg active ingredient; 10 mL/kg solution

Test method: OECD TG 401 (limit test)

Mortality: no deaths occurred during the study

Clinical observations: no clinical signs of toxicity were observed

Morphological findings: no gross abnormalities were observed at necropsy

 LD_{50} : > 2000 mg/kg

Result: the notified polymer was of very low acute oral

toxicity in rats

9.2 Overall Assessment of Toxicological Data

The notified polymer was found to be of very low acute oral toxicity in rats. No other toxicological data were submitted. However, the notified polymer contains a high level of epoxy oligomers derived from phenol, 4,4'-(1-methylethylidene)bis-, polymer with (chloromethyl)oxirane, (CAS No. 25068-38-6) including the monomer oxirane, 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxy methylene)]bis- (bisphenol A diglycidyl ether). The oligomers are classified as hazardous substances, with risk phrases R36/38 "Irritating to eyes and skin" and R43 "May cause sensitisation by skin contact" for oligomers of molecular weight \leq 700 (NOHSC, 1999a). The monomer, bisphenol A diglycidyl ether, has the same classification.

The epoxy oligomers are reported to be moderately toxic by ingestion and skin contact, with an oral LD₅₀ in rats of 1100 mg/kg, and a dermal LD₅₀ in rabbits of > 20 mL/kg (Sax & Lewis, 1996).

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The notifier has provided the following ecotoxicological data.

Species	Test	Concentrations	Result	Reference
Water Flea (Daphnia magna)	48 h acute	13, 22, 36, 60 and 100 % of 100 mg of active ingredient/L	•	(Collins, 1997)
Algae (Selenastrum capricornutum)	96 h growth	3.1, 6.3, 13, 25, 50 and 100 mg of active ingredient/L	$EC_{50} = 79 \text{ mg/L}$ $NOEC = 13 \text{ mg/L}$ $E_BC_{50} = 79 \text{ mg/L}$ (72 hrs)	(Hoberg, 1997)

OECD Guideline 202 was followed for the acute toxicity test to daphnia. The test was conducted in quadruplicate under static conditions in 250 mL glass beakers with 200 mL of test solution and 5 daphnia added to each beaker. The test solution was prepared by adding 547.1 mg of notified polymer to 4 L of dilution water, stirring for 18 hours and standing for 1 hour. Following standing, undissolved test material was observed at the bottom of the vessel. The supersaturated solution in the vessel was siphoned off and used as the stock solution. The stock solution was diluted as required for the desired test concentrations. Immobilisation and physical observations of the daphnia, along with pH and dissolved oxygen measurements on the test solutions, were taken at 0, 24 and 48 hours. In one replicate the temperature was measured at 0, 24 and 48 hours, while in the other replicates the temperature was measured continuously. A solvent blank and a dilution water control were treated in the same manner. As no effects on daphnia were noted, the EC₅₀ was determined to be greater than 100 mg/L for the supersaturated test solution.

OECD Guideline 201 was followed for the 96 hour algal toxicity test. The test was conducted in triplicate under static conditions in 250 mL Erlenmeyer flasks with 100 mL of test solution. The test solution was prepared by dissolving 136.1 mg of notified polymer in 1 L of algal medium, prepared with deionized water. At this stage, undissolved test material was observed at the bottom of the vessel. The solution was heated for two hours at 64°C, cooled and stirred for 24 hours, allowed to settle, and the supersaturated solution was siphoned off. Each flask was inoculated with 0.3 mL of *Selenastrum capricornutum* cells to give a cell density of approximately 1.0×10^4 cells/mL. The test was conducted in an environmental chamber so as to maintain the following parameters: 24°C temperature, 300-500 footcandle continuous light intensity and 100 rpm shaking rate. Cell counts and cell health observations were made every 24 hours. Dilution water controls were treated in the same manner. An EC₅₀ of 79 mg/L for the supersaturated solution was estimated.

As measurements of total organic carbon content in the supersaturated solutions were not made, the best that can be concluded is that the polymer is not toxic to the limit of its water solubility to daphnia, but does exhibit some toxicity to algae.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Once the paint is applied and cured, the polymer will crosslink with the other components to

form a stable coating and consequently should not present a hazard. Any chips, flakes or fragments formed by mistreatment or general wear and tear will be inert. The coating will slowly deteriorate due to exposure to UV light and the other elements, but this will be insignificant, particularly as the notified polymer will be covered by several paint layers.

Waste generated during the manufacture and use of the coating will be disposed of to landfill or by incineration. The monomers and oligomers associated with the polymer may leach from a landfill. However, this will be in very low concentrations and in a diffuse manner.

From the ecotoxicity data provided, it may be concluded that the polymer is not toxic to the limit of its water solubility to daphnia, but is toxic to algae.

This notified polymer is not likely to pose an environmental hazard when used under the conditions specified.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Limited toxicological information has been provided for the notified polymer and therefore the substance cannot be classified in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b). The acute oral toxicity of the notified polymer is very low. The systemic toxicity of a polymer with molecular weight greater than 1000 is generally low due to its high molecular weight and consequent low bioavailability. However, the presence of a high level of low molecular weight epoxy oligomers (> 40 % species with MW < 1000, equivalent to \sim 14 % in the solution) in the notified polymer will result in increased bioavailability and toxicity.

The oligomers are hazardous substances, with health effects including skin and eye irritation and skin sensitisation. The polymer solution contains an epoxy monomer (oxirane, 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxy methylene)]bis-, or bisphenol A diglycidyl ether) which is a hazardous substance, with health effects including severe skin and eye irritation and skin sensitisation. The risk phrases R36/38 and R43 are applied to both the oligomers and the monomer at the levels present in the notified polymer and the solution. The notified polymer is therefore classified as a hazardous substance, with the risk phrases R36/38 and R43.

The polymer solution HE-76-1788 is a hazardous substance due to the concentration of xylene (60.4 %), epoxy oligomers (~ 14 % in the solution) and bisphenol A diglycidyl ether (5.6 %). It is also a Class 3 dangerous good (flammable liquid) due to the solvent content. The Material Safety Data Sheet (MSDS) for the polymer solution HE-76-1788 lists a number of potential health effects, namely headaches, dizziness, nausea, vomiting, skin, eye and respiratory irritation, skin degreasing, skin sensitisation, central nervous system depression and chronic central nervous system disorders. It is also an aspiration hazard if swallowed. The potential health effects relate to the solvents, n-butanol and xylene, and also the impurity bisphenol A diglycidyl ether and epoxy oligomers.

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 reformulation of the polymer solution and use and disposal of the paints.

The solution, HE-76-1788, containing the notified polymer, is a hazardous substance with health effects including skin and eye irritation and skin sensitisation. Engineering controls should be selected to minimise exposure to the resin solution during reformulation, and where exposure may occur, personal protective equipment including eye protection and impervious gloves should be used.

The paint containing the notified polymer at < 10 %, is also a hazardous substance due to the concentration (> 60 %) of xylene. The paint is applied by a spraying procedure which produces a dense aerosol of paint particles, increasing the exposure to the hazardous components. The presence of 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 should provide adequate protection from the notified polymer.

Once the applied final paint mix has hardened and been covered by additional paint layers, the polymer will not be separately available for exposure or absorption.

There are NOHSC exposure standards for n-butanol and xylene, identified as ingredients in the polymer solution HE-76-1788, and methyl n-amyl ketone, an additional ingredient in the finished paint. The employer is responsible for ensuring that these exposure standards, and exposure standards pertaining to other final paint mix additives, are not exceeded in the workplace.

The paint components containing the notified polymer are flammable due to their solvent content. Precautions must be taken to avoid sources of ignition, e.g. use of earthing leads. Operators should wear antistatic overalls and footwear.

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.

Public Health

There is negligible potential for public exposure to the notified polymer arising from use in paints. There may be public contact with the notified polymer on the painted surfaces of motor vehicles, but its adhesion to the substrate and the physico-chemical properties of the cured paint will be sufficient to preclude absorption across the skin or other biological membranes. In addition, the notified polymer will be contained in an underlying layer which will be covered by additional paint layers. Therefore, based on its use pattern, physico-chemical characteristics and likely low toxicity, the notified polymer will not pose a significant hazard to public health.

13. RECOMMENDATIONS

To minimise occupational exposure to HE-76-1788 the following guidelines and precautions should be observed:

- Use of the paint containing the notified polymer should be in accordance with the NOHSC *National Guidance Material for Spray Painting* (NOHSC, 1999c);
- Employers should ensure that NOHSC exposure standards for all of the components of the polymer solution (when imported) and the final paint mix are not exceeded in the workplace;
- Safety goggles should be selected and fitted in accordance with Australian Standard (AS) 1336 (Standards Australia, 1994) to comply with Australian/New Zealand Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand, 1992); industrial clothing should conform to the specifications detailed in AS 2919 (Standards Australia, 1987) and AS 3765.2 (Standards Australia, 1990); impermeable gloves or mittens should conform to AS 2161 (Standards Australia/ Standards New Zealand, 1998); all occupational footwear should conform to AS/NZS 2210 (Standards Australia/ Standards New Zealand, 1994);
- 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 the conditions of use are varied from the notified use (as a coating for automobile bodies), greater exposure of the public may occur. In such circumstances, secondary notification may be required to assess the hazards to public health.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, secondary notification of the notified chemical shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. Secondary notification under Section 64 of the Act will be required if the method of use changes in such a way as to greatly increase the environmental exposure of the notified polymer, particularly to natural waters, or if additional information becomes available on adverse environmental effects of

the polymer. No other specific conditions are prescribed.

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