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August 1999

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Polymer in WE-17-5607

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**Polymer in WE-17-5607****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 WE-17-5607.

2. IDENTITY OF THE CHEMICAL

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

Marketing Name: WE-17-5067
WE-46-1329
WE-87-2424
WE-84-1554
E6110, E6102, E6116A, E6116, E6214, E6126

Other Names: PMN 1844

3. PHYSICAL AND CHEMICAL PROPERTIES

The notified polymer will be imported to Australia in the form of an aqueous dispersion containing a high proportion of polymers. The polymer will not be isolated and therefore the physical and chemical properties reported below are those of a 30.9 % (w/v) aqueous polymer dispersion except where otherwise indicated.

**Appearance at 20°C
and 101.3 kPa:** viscous liquid

Melting Point: not determined (see comment below)

Specific Gravity: 1.08

Vapour Pressure:	2.3 kPa at 25°C
Water Solubility:	< 10 mg/L at 25°C and pH 7 48.5 mg/L at 25°C and pH 1 14.2 mg/L at 25°C and pH 10
Partition Co-efficient (n-octanol/water):	$\log P_{ow} < -0.15$ (see comments below)
Hydrolysis as a Function of pH:	not determined (see comments below)
Adsorption/Desorption:	not determined (see comments below)
Dissociation Constant:	not determined (see comments below)
Flammability Limits:	not combustible
Explosive Properties:	not explosive
Reactivity/Stability:	not expected to be reactive under normal conditions

Comments on Physico-Chemical Properties

The notifier indicated that due to the polymer never being isolated from the aqueous environment in which it is prepared, definitive melting point data is not available. It was suggested that if prepared in pure form, the polymer would soften and flow over a wide temperature range.

The high molecular weight of the polymer suggests low vapour pressure.

Water solubility was determined using an HPLC method at pH 1, 7 and 10 using appropriate aqueous buffer solutions. The method used involved taking aliquots of the polymer dissolved in dimethylformamide (DMF) and adding to around 60 mL of the appropriate buffer such that the nominal concentration was around 1200 mg/L. Following this, the flasks were shaken for 24 hours in a water bath at 30°C, and then allowed to equilibrate at 20°C prior to being centrifuged to separate solid (undissolved) material. The aqueous phases were then filtered through 0.45 micron filters, and the resultant solutions then evaporated to dryness. The recovered solid polymer was then taken up in DMF and analysed using HPLC. The results indicated overall low water solubility, with the solubility at pH 1 being 48.5 mg/L, while that at pH 10 is 14.2 mg/L. At pH 7 the solubility was found to be < 10 mg/L.

Although the low water solubility determined in this manner is consistent with a high molecular weight polymer containing few hydrophilic groups, the notifier indicates that the polymer will be imported and used as an aqueous dispersion with high solids content

(23.3 %). It was indicated that the polymer molecules in this dispersion are effectively in the form of micelles (presumably stabilised by the positive charges on the amine groups). However, it is possible that the dispersion is further stabilised by the presence of surfactants or other species, but no mention of such adjuvants was made in the notification.

The solubility of the polymer in n-octanol was determined as < 44.8 mg/L (44.8 mg/L was the quantifiable detection limit of the available method) using UV-visible spectroscopy.

The n-octanol/water partition coefficient was not determined, but can be estimated from the ratio of the solubility in n-octanol to that in water. At pH 1 this indicates that $P_{ow} < 0.21$ ($\text{Log } P_{ow} < -0.68$), while at pH 10 the estimate is < 0.7 ($\text{Log } P_{ow} < -0.15$). Suitable quantified solubility data does not exist for estimation at pH 7, but a low value for $\text{Log } P_{ow}$ could also be expected here. This solubility and partition coefficient data indicates that the polymer has little affinity for either the oil or the aqueous phases.

Adsorption/desorption data was not presented in the submission, but the positive charges on the ends of the polymer chain (see below) indicate that if spilled onto soils, the polymer may associate with the surface of negatively charged clay minerals. In this situation adsorption to the mineral surfaces is not expected to be very strong, but due to the low water solubility, high mobility of the polymer through the soil would not be expected.

The polymer is terminated at both ends by amino groups. No pK_a data was provided but both amine groups could be expected to behave as typical aliphatic amines and be appreciably basic. Consequently, both would be protonated and carry positive electrical charge in the usual environmental pH region where $4 < \text{pH} < 9$.

4. PURITY OF THE CHEMICAL

Degree of Purity: < 26 % in aqueous dispersion

Maximum Content of Residual Monomers: All residual monomers are present at < 1 %, and hazardous residual monomers are present below the respective cutoff levels for classification of the polymer as hazardous. Other reactants used in forming the final polymer are also below the respective cutoff levels for classification of the polymer as hazardous.

Additives/Adjuvants:

The notified polymer will initially be imported in pre-prepared binder resin, and will have a variety of adjuvants including additional resins and solvents. A number of the components of the imported products are specified in the Material Safety Data Sheet (MSDS).

5. USE, VOLUME AND FORMULATION

The notified polymer will not be manufactured in Australia. Initially, it will be imported as part of an aqueous coating resin formulation at a concentration of less than 20 % (w/v). Later it will be imported as a resin dispersion at a concentration of up to 26 % (w/v) and blended locally to produce the aqueous coating resin formulation. The formulated product will be diluted by approximately a factor of two prior to end use. The coating resin and the resin dispersion will be imported in 200 L drums or 1000 L tote tanks.

The polymer will be used as a binder resin in an electrodepositable coating composition used as a primer coating for automobile bodies in an immersion bath. The polymer will only be used in automobile assembly plants.

The import volume within the first five years will be a maximum of 375 tonnes per annum.

6. OCCUPATIONAL EXPOSURE

Transport and Storage

The notified polymer as part of a formulated aqueous coating resin product will be transported from the docks to the notifier's warehouse, where it will be distributed to the 13 possible customer sites in Australia. After the first year, the notified polymer will be imported as a 26 % aqueous dispersion for local blending. The blended product will then be delivered by tanker to the customer sites. The notifier expects that 2 waterside workers and 2 warehouse workers, along with an unspecified number of transport drivers, will handle the containers of the coating formulation or resin dispersion containing the notified polymer, for approximately 4 hours, 60 times a year. The original containers will not be opened, so it is unlikely that these workers will be exposed, except in the event of an accident involving the rupture of a drum or tank.

During tanker transfer, there is possible exposure of drivers and storage workers being exposed to drips and spills containing the notified polymer while connecting and disconnecting transfer hoses.

Reformulation

The blending operation, when commenced, will be carried out in a sealed, automated blending system. The imported resin dispersion, containing up to 26 % notified polymer will be pumped from the import containers into the sealed blend tank and mixed with water and other ingredients to produce the formulated aqueous coating resin product, containing up to 20 % notified polymer. The reformulated product will be pumped to a storage tank, and then to delivery tankers.

The notifier estimates that 2 plant operators and 1 laboratory worker will be involved in handling the notified polymer in this operation. The exposure is estimated to be for 4 hours per day, 200 days per year.

Dermal exposure to drips and spills containing the notified polymer will be possible when containers are exchanged and transfer hoses connected and disconnected. The product will be sampled through sampling valves, and dermal exposure is also possible at this time, as well as during laboratory testing.

The notifier states that workers handling the notified polymer during this process would wear impervious gloves, coveralls and goggles.

Primer Application

The notified polymer in the formulated aqueous coating resin product is used in a section of the automated production line in automobile assembly plants. The electrodeposition process involves the use of a potentially dangerous electric current in a wet environment, so the plant operators and the bath containing the notified polymer are physically separated during the normal operation of the production line.

The notifier estimates that 2 plant operators per shift will be exposed to the notified polymer at each production facility. The exposure is estimated to be for 2 hours per shift, 250 times per year.

The product containing the notified polymer will be transferred, using a coupling hose, from the delivery tanks to customer storage tanks, from which it will be dispensed into a large water bath via an automated transfer system. There is possibility of dermal exposure to drips and spills when the containers are exchanged and the transfer hoses are disconnected and reconnected. Alternately, the product can be pumped from the imported drums directly into the water bath by drum lance. This transfer may also involve potential dermal exposure to drips and spills.

The automobile bodies are lowered into the water bath by the production line conveyor until completely submerged; a negative voltage is then applied and the electrostatically charged paint is deposited onto the body. The conveyor then lifts the automobile body out of the bath and excess polymer solution is washed off back into the bath with water; the concentration of the bath is maintained as the wash water is recirculated from the bath through an ultrafiltration system. The automobile body is then transferred by conveyor to a baking oven, where the crosslinking reaction occurs. After this process, the polymer coating is crosslinked and the notified polymer is no longer separately available for exposure.

There is a need for periodic sampling and testing of the bath contents to ensure that the concentrations of all of the paint components, including the notified polymer, are maintained. Dermal exposure of plant operators to the bath contents is possible during sampling. The laboratory staff who test the samples may also come into dermal contact with the notified polymer.

Exposure during disposal and plant cleaning is unlikely, as the process is continuous with no buildup of impurities which would require the changeover of bath solutions. The notifier states that changing from one electrodeposition paint system to another would be done by

adding the new paint materials when topping up the bath contents, so that the bath contents would be gradually changed and no cleaning and disposal would be required.

The bath containing the notified polymer is enclosed and local exhaust ventilation is used to remove any solvent vapours which may be present.

Plant operators would be expected to wear gloves, protective eyewear and clothes, and other personal protective equipment as required.

7. PUBLIC EXPOSURE

The notified polymer will only be used by industrial automobile manufacturers, and is not available to the general public. Once applied to the automobile body, the notified polymer is bound in an insoluble polymeric matrix, and not separately available for exposure. In addition, it will be covered by several layers of paint. Consequently, the potential for public exposure to the notified polymer through all phases of its life cycle is considered to be negligible.

8. ENVIRONMENTAL EXPOSURE

Release

There is potential for release of the notified polymer by accidental spillage during transfer of the imported dispersion to the enclosed blending system at the notifier's plant. Potential for spillage also exists when transferring the blended product from the storage tank to delivery tankers. Such spills will be contained to the plant by existing bunding, and collected by licensed waste disposal contractors.

The hoses, pumps and tanks used during the blending process are rinsed with water and the rinsate is returned to the process. Very little waste is therefore produced during the blending process.

The notifier estimates that 2500 kg per annum of residue will remain in the empty containers after use, and 150 kg per annum of residue from test samples will occur. A further 625 kg per annum may result from spills during local blending operations.

The majority of the aqueous coating resin product will be delivered to the customers in bulk in returnable tanks and transferred to the customer's storage tank using a coupling hose. The returnable tank and hoses will be rinsed with water and the rinsate added to the storage tank. There is potential for release of the notified polymer by accidental spillage at this stage. Such spills would be contained by bunding, and would be collected by licensed waste disposal contractors. The notifier estimates that a further 625 kg per annum of notified polymer may be released in this way.

It is likely that the release estimates provided by the notifier are low, and a reasonable estimate would be 3.5 % of the imported volume (spillage 1 %, cleaning 1 % and residue 1.5 %). This would result in the release of approximately 13.1 tonnes of notified polymer per annum.

Due to the manner in which the new polymer is used, very little release of the liquid polymer formulation is anticipated during application to the vehicle bodies. The notifier has indicated that any spills that occur during this process are contained within bunded areas and collected by licensed waste disposal contractors. After collection, this waste (presumably combined with other liquid wastes) is treated by flocculation, filtration and centrifugation, which separates the solid polymeric material from the water. The water is discharged to sewer, while the solid sludge is dried and sent to a secure landfill. Empty drums are sent to a drum recycler and are cleaned by incineration.

The company also indicated that the large electrodeposition tanks are cleaned approximately every two years. This process involves pumping the tank contents to reserve storage vessels, and rinsing the tanks out with water. The rinse water and entrained sludge from the bottom of the tanks is collected by licensed waste contractors and treated in a similar manner to spills.

It was also indicated in the notification that some fugitive vapours (probably including the neutralising acid) are released from the primer during the curing process as the vehicle bodies pass through the ovens. However, these are destroyed in an afterburner which operates at 760°C.

After the polymer has been cross linked into the paint matrix, there is little possibility for release, and even if this did occur it would be in the form of inert flakes of cured (cross linked) paint.

Fate

Most of the new polymer becomes associated with a durable paint film on the metal surfaces of motor vehicles, and consequently the fate of the majority of the material will be similar to that of the car bodies themselves. This is likely to be either recycling for recovery of the metals, or deposition into landfill.

During the recovery of the metals, the organic paint coatings would be destroyed as a result of the high temperatures in the blast furnaces, and the polymer would be decomposed to water vapour and oxides of carbon and nitrogen. Any material incinerated as a consequence of trade waste disposal operations would be destroyed in a similar manner.

The polymer is not readily biodegradable and a CO₂ evolution test (Harris, 1995) with domestic sewage sludge bacteria (Modified Sturm Test, OECD TG 301B) indicated only around 5 % degradation over a 29 day period compared with the control substance, sodium benzoate which was degraded to around 90 %. In this study, a parallel abiotic control indicated only 0.8 % degradation over the 29 day period. These tests indicate that the

polymer is stable to both biological and abiotic processes. However, in a landfill the cured paint film containing the notified polymer would be expected to be very slowly degraded as a consequence of micro-biological processes with release of gases such as carbon dioxide, methane, ammonia and nitrogen.

No release of the polymer to the water compartment is expected, except possibly as result of transport accident. However, in event of such an accident, bioaccumulation of the polymer would be unlikely due to the difficulty for high molecular weight molecules in crossing biological membranes.

If the uncured polymer was released to the soil as result of accidental spills, it would be expected to become associated with the surface of clay minerals, but due to the low water solubility is not expected to be mobile in soil.

9. EVALUATION OF TOXICOLOGICAL DATA

There is no toxicity data on the notified polymer. Data are available for a 30.9 % aqueous dispersion (referred to PMN 1844). The dose was corrected for the concentration of active ingredient.

9.1 Acute Toxicity

9.1.1 Oral Toxicity (Naas, 1994)

<i>Species/strain:</i>	rat/Crl:CD [®] BR
<i>Number/sex of animals:</i>	5/sex
<i>Observation period:</i>	14 days
<i>Method of administration:</i>	gastric intubation; 30.9 % aqueous dispersion
<i>Dose:</i>	single dose, 2000 mg/kg
<i>Test method:</i>	OECD TG 401
<i>Mortality:</i>	there were no deaths during the study
<i>Clinical observations:</i>	mucoïd faeces and wet yellow urogenital staining on the day of dosing; no other clinical signs of toxicity
<i>Morphological findings:</i>	there were no gross pathological changes observed
<i>LD₅₀:</i>	> 2000 mg/kg

Result: the notified polymer was of very low acute oral toxicity in rats

9.2 Overall Assessment of Toxicological Data

The acute oral toxicity of the notified polymer is very low. No reports of dermal or inhalation toxicity or skin irritation or sensitisation were provided by the notifier, which is acceptable for a limited notification of a polymer with NAMW > 1000.

Polymers of high molecular weight do not readily cross the skin or other biological membranes, and the overall toxicity is expected to be low. The notified polymer will have surfactant properties and could be a skin irritant through skin defatting. It is also potentially basic or acidic, depending on the conformation of the polymer in the micelles, and could have skin and eye irritant properties associated with the pH of the aqueous polymer dispersion.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

While not required by the Act for polymers assessed as Limited Notifications, the company provided the following ecotoxicity data for PMN 1844, containing the new polymer.

<i>Test</i>	<i>Species</i>	<i>Results</i>
acute immobilisation (Sword, 1995)	<i>Daphnia magna</i>	EC ₅₀ (48 h) = 23 mg/L NOEC (48 h) = 0.23 mg/L
bacterial respiration	sewage bacteria	no toxic effects noted

* NOEC - no observable effect concentration

The tests on *Daphnia magna* were conducted with solutions of the polymer containing nominal concentrations of 0.23, 0.45, 0.91, 1.8, 3.6, 7.3, 15, 29, and 58 mg/L, together with a control containing no test substance. Samples of some of the solutions were taken at 0 and 48 hours after the start of the test and analysed for polymer content, and the measured concentrations were within the range 74 % ± 24 % of the nominal concentrations. Each test was performed in quadruplicate, using 5 animals in each test vessel (ie 20 daphnids per test concentration). Temperature was maintained at 20 ± 2°C, and water hardness, pH and dissolved oxygen levels were between 130 and 160 mg/L (as CaCO₃), 7.9 and 8.6 and 3.3 and 8.5 mg/L respectively.

After 48 hours exposure to a nominal 0.45 mg/L of polymer, 4 (of 20) of the daphnia were immobile on the bottom of the test vessels, and at higher exposures the animals were coated with or trailed extraneous material, or were quiescent (immobilised).

The data was analysed using the computer program developed by Stephan et al (1978), which calculates the EC₅₀ concentration and 95 % confidence interval using the binomial, moving average and probit tests. These data furnished a nominal EC₅₀ value of 23 mg/L (95 % confidence interval 15 – 29 mg/L) with a NOEC of 0.23 mg/L. However, based on the

measured solute concentrations, the EC₅₀ was 14 mg/L.

These results indicate that the polymer is slightly toxic to this species. Although test reports on the acute toxicity to fish and on inhibition of algal growth were not provided, it is likely that the polymer would exhibit at least similar toxicity to these species.

No specific test on inhibition of bacterial respiration was conducted, but a toxicity control conducted as part of the test of ready biodegradation (Modified Sturm Test – see above) indicated that no toxic effects were observed when bacteria were exposed to the polymer at levels equivalent to 40 mg/L of organic carbon.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The environmental hazard resulting from the intended use of the notified polymer appears to be low.

Most of the polymer will remain as part of a highly cross linked paint coating on the metal surfaces of vehicle bodies. At the end of their serviceable lives, vehicle bodies coated with primer containing the notified material would be either recycled for metal recovery, or possibly placed into land fills. During the smelting of old vehicle bodies for metal recovery the polymer would be decomposed to water vapour and oxides of carbon and nitrogen. Any polymer incinerated as a result of industrial waste disposal practices would be decomposed in a similar manner. Some polymer may be placed into landfill, either as a coating on old vehicle parts or as a result of waste disposal from spillage or other losses (this is estimated to be < 5 % of total imports). Although not biodegradable, the polymer is expected to be very slowly degraded over a prolonged period through the agency of various abiotic and biological processes, again producing water and oxides of carbon and nitrogen.

Although the polymer is slightly toxic to *Daphnia magna* (48 h EC₅₀ = 14 mg/L with a NOEC of 0.23 mg/L), and presumably toxic at similar levels to other aquatic species, it is unlikely that it would be released into the water compartment in a non cross linked form. Consequently, the risk to the aquatic environment from normal use of the polymer is assessed as low.

The polymer is not expected to be mobile in the soil compartment, and is unlikely to bioaccumulate.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Little toxicological data has been provided and the notified polymer cannot be assessed against the NOHSC *Approved Criteria for Classifying Hazardous Substances* (National Occupational Health and Safety Commission, 1994b). The notified polymer is of very low oral toxicity. Polymers of high molecular weight do not readily cross the skin or other

biological membranes, and the overall toxicity is expected to be low. The concentrated solutions of the polymer has surfactant properties and could be a skin and eye irritant, as indicated in the MSDS.

Occupational Health and Safety

There is little potential for significant occupational exposure to the notified polymer in the transport and storage of the resin dispersion and the primer components containing this polymer.

The blending system in which the primer component is manufactured is enclosed and exposure to the notified polymer is only likely when containers are coupled and uncoupled from the blending system, and when samples are removed from the blend tank for testing.

The system by which the primer component is dispensed and used is enclosed, and exposure to the notified polymer is only likely when containers are coupled and uncoupled from the production line, and when samples of the electrodeposition bath are removed for testing to allow the concentration of polymer in the bath to be maintained. In normal operation, the electrodeposition bath containing the notified polymer will be completely enclosed due to the electrocution hazard associated with the electrodeposition process.

Plant operators and laboratory staff who may come into contact with the notified chemical should take adequate precautions, including the wearing of protective clothing, eyewear and gloves to prevent dermal or ocular exposure.

Public Health

There is negligible potential for public exposure to the notified polymer arising from use in automobile primers. There is little chance of public contact with the notified polymer in the lower paint layers of motor vehicles, and its adhesion to the substrate and the physico-chemical properties of the cured primer will be sufficient to preclude absorption across the skin or other biological membranes. Therefore, based on its use pattern and physico-chemical characteristics, the notified polymer will not pose a significant hazard to public health.

13. RECOMMENDATIONS

To minimise occupational exposure to Polymer in WE-17-5607 the following guidelines and precautions should be observed:

- Employers should ensure that NOHSC exposure standards for all of the components of 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 use by industrial automobile manufacturers, greater exposure of the public to the notified polymer may occur. Under such circumstances, further information 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* (National Occupational Health and Safety Commission, 1994a).

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.

16. REFERENCES

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Naas, D. J. (1994) Acute Oral Toxicity Study of PMN 1844 in Albino Rats, Project No. 41443, WIL Research Laboratories, Ashland, Ohio, USA

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C.E. Stephan, K.A. Busch, R. Smith J. Burke and R.W. Andrews (1978) A Computer Program for Calculating an LC₅₀, U.S. Environmental Protection Agency, Duluth Minnesota, pre-publication manuscript August 1978

Sword, M. C., Bussard, J. B., March, K. L. & Bucksath, J. D. (1995) Static Acute toxicity of PMN 01844 to *Daphnia magna*, Project No. 42198, ABC Laboratories, Columbia, Mo, USA